

PHOSPHATE BONDED SILICON CARBIDE REFRACTORIES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
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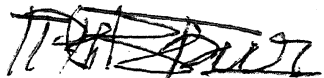
DEPARTMENT OF METALLURGICAL ENGINEERING
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APRIL, 1985

CERTIFICATE

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Kausik Bandyopadhyay

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body as a function of the amount of
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with (a) 1 Ton moulding pressure and
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ABSTRACT

Silicon carbide, a very hard and abrasive material, was used to develop a strong, abrasion resistance refractory body. The silicon carbide aggregates were bonded with either 75% fine SiC and 25% calcined talc powder or 75% fine SiC and 25% thermit slag powder matrices mixed with phosphoric acid. High ^{tensile} strengths of around 150 Kg/cm^2 were obtained after firing at a relatively low temperature of 800°C . This phosphate bonded silicon carbide body can be used as rubbing stones, abrasion resistance liners for hydrocycloners, ash discharge gate and heat exchangers etc.

CHAPTER-I

INTRODUCTION

Severe service conditions of erosion, corrosion and mechanical stresses exist in industrial furnaces. Varied and newer demands are placed on refractory items with respect to their performance behaviour. These also need for ceramics which can be shaped cold, and on the application of moderate heat form a strong, dense body with minimum shrinkage.

The high cost of firing of refractory items is a major economic disadvantage particularly in view of the price escalation of petroleum oils and other fuels. This has ushered in a new era for the development of refractory items which can be produced at lower processing temperatures and thereby saving energy but at the same time not surrendering their strategic property parameters.

Various attempts were made to attain these goals, perhaps the most promising one is the development of chemical bonds at low curing temperatures. A commonly used chemical bond is the phosphate bond. Thermosetting phosphate bonded alumina refractories, owing to their useful properties, have achieved success in steel plants in such vital areas as hot metal transfer ladles, soaking pit slaglines and blast

furnaces¹. Phosphate bonded burnt high Al_2O_3 (85%) bricks have found use in the lower stack lining of blast furnaces since they are dense and strong and have low permeability and resist penetration of gases carrying alkali and carbon monoxide, and the rate of reaction of these gases with the lining. The brick can also be used below wear plates at the upper stack due to their excellent wear resistance to the charging of burden into the furnace². They have also performed well in non-ferrous metallurgical applications such as hearths and lower side walls of aluminium re-melting and holding furnaces³.

Phosphate bond is added with corundum ramming mixtures and castables to be used as rails in pusher type furnaces and with zirconia and silicate bodies which have to withstand severe stresses due to thermal shock⁴.

Phosphate bonded high Al_2O_3 bricks and ramming compositions cured only at lower temperatures are suitable also for electric arc furnace roofs since this product has high cold crushing strength, accurate dimensions and good slag and abrasion resistance properties⁵.

Phosphate bonded high aluminas are effective lining materials for the fluidized bed reactors for coal gasification. Process atmosphere corrosion is one specific

problem for coal gasification refractories which has been successfully solved by the phosphate bonded aluminas as they have good resistance to atmosphere of hydrogen, steam, carbon monoxide and dioxide ⁶.

All-magnesite phosphate-bonded brick has been used in open hearth, basic oxygen and electric arc furnaces. In open hearth walls, service is generally satisfactory, comparable to direct bonded brick. Its performance in copper reverberatory roof is excellent. The improved phosphate bonded all-magnesite dry gunning mixes have been technically successful in the maintenance gunning of basic oxygen and electric arc furnaces.

Unlike phosphate bonded alumina refractories very little information is available on phosphate bonded silicon carbide refractories which can be used for machine gunning (i.e. lining) the pivot screens of the fireboxes of steam boilers⁷, heat exchangers, muffle and hot zones subject to severe abrasion conditions.

This study was initiated to find out a suitable phosphate bond and bond matrix for silicon carbide refractories which can be cured at relatively lower temperatures to give a dense, strong and dimensionally stable product.

CHAPTER - II

LITERATURE SURVEY

1. GENERAL

In 1950 Kingery⁸ summarized the literature on phosphate bonding. In refractory applications, bonding is accomplished by three major methods:

(i) The use of siliceous materials with phosphoric acid-suitable heat treatment is generally necessary for development of any reasonable strength.

(ii) The use of oxides and phosphoric acid to form either cold-setting or heat-setting bonds.

(iii) Direct addition or formation of acid phosphates.

Kingery studied the reactions and properties of cold setting phosphoric acid bonds with metal oxides and hydroxides. His experimental data indicates that formation of acid phosphates is responsible for bond formation at room temperature.

The above three methods are still widely used, although other phosphate bonding agents are now also known, viz., ammonium phosphate, chromium-aluminium phosphate,

aluminium chlorophosphate hydrate, alkali metaphosphates and mixtures of aluminium phosphate hydrate and urea phosphate⁹. Phosphoric acid and solutions of monoaluminium phosphate (MAP) are the most extensively used bonds for various refractories whose properties are significantly influenced by the physico-chemical nature of the phosphate bond employed.

2. CHEMISTRY OF PHOSPHATE BONDING

(A) PHOSPHORIC ACID:

The oxide-phosphoric acid reactions at room temperature may be divided into three classes. Oxides of an acidic or chemically inert nature do not react with phosphoric acid. Oxides of a highly basic nature react so violently that a porous and friable structure results. Phosphoric acid reacts with many oxides of weakly basic or amphoteric nature, but not all of these form bonding products. Of the hardening systems based on H_3PO_4 and Al_2O_3 , Cr_2O_3 , ZnO , which are known, the most extensively studied system is $\text{H}_3\text{PO}_4 - \text{Al}_2\text{O}_3$.

Literature data on the reaction of phosphoric acid with alumina are numerous and contradictory. Aluminium is known to be capable of forming different solid phases with phosphates depending on the initial concentration of the two reactants and the pH. Because of the close similarity in their chemical properties, and the complex procedure needed

for their preparation and separation, it is not easy to identify different phases.

Sheets et al¹⁰ concluded that the phosphate bonding in high alumina refractories occurs because of covalent polymerisation of aluminium phosphates, which proceeds in several stages on heating. According to them the phosphate bonding can be viewed as a heteropolyanionization process leading to the formation of strong oxygen polyhedral structure. In this picture of bonding, the factors influencing the strength of the bond are the water content of the original batch, availability of aluminium cation, temperature, rate of drying and amount of impurities. These authors, while making castable refractories (i.e. compositions that set without firing) using phosphoric acid, introduced the concept of adding an inhibitor: Rodine 78, a complex amine, to reduce the phenomenon known as bloating which results from the reaction between phosphate and metallic iron. They found that it was not possible to get a cold set using mixtures of phosphoric acid and alumina grog with either fine reactive alumina, or hydrated alumina, these compositions had to be dried. However, the addition of ammonium fluoride enabled a cold-setting mixture to be formed.

Klyucharev and Skoblo¹¹ claim that ambient temperature setting is due to the formation of variscite

($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) whereas setting during heating is due to the formation of an amorphous phase. This theory is in agreement with the solubility studies in the system $\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ under the condition of excess alumina ^{12,13}.

Kopeikin et al ¹⁴ and Yutina et al ¹⁵ maintain that the ability of mixes containing orthophosphoric acid and alumina to acquire strength and moisture resistance when heated to 270°C is not due to the formation of anhydrous AlPO_4 in any of its various polymorphic forms, but rather due to the formation of an amorphous phosphate.

Many investigators ^{11,14,15} have suggested that the formation of phases by the phosphoric acid - alumina reaction is similar to those formed by the phosphoric acid-aluminium hydroxide reactions.

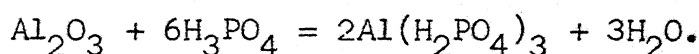
The usual procedure has been to assume that whatever changes occur in certain aluminophosphate binders or binders with small additions of aluminium hydroxide will also occur in the orthophosphoric acid-alumina mixes because of the relative inertness of alumina.

The review paper by Cassidy ¹⁶ points out that in real refractory systems an excess of some reactive phase such as alumina, silica, zirconia, etc. is always present. Thus

bonding occurs in two ways: by chemical bonding to the aggregate and by the formation of acidic or condensed phosphates, which at certain temperatures may decompose into polymeric phosphates which are mostly amorphous. The work of O'Hara et al ¹⁷ shows this feature very clearly. The drop in strength observed in some phosphate bonded high alumina refractories has been attributed by these investigators to the recrystallization of the amorphous phases which takes place at still higher temperatures, and is accompanied by liberation of P_2O_5 .

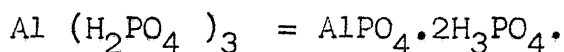
The chemical reaction between alumina and orthophosphoric acid can be summarized according to a recent paper of Gonzalez and Halloran ¹⁸.

At the beginning and at moderately low temperature the reaction is viewed as the dissolution of alumina ions into the acids in several steps: transport of the reactant to the interface, reaction at the interface, and transport of the product away from the interface. The reaction certainly yields the primary soluble phosphates $Al (H_2PO_4)_3$, according to,

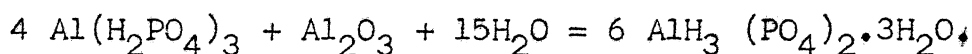


However, solutions of monoaluminium phosphate are unstable and $Al(H_2PO_4)_3$ should be considered as an acidic

salt of aluminium orthophosphate with two loosely attached molecules of orthophosphoric acid ^{12,19}.

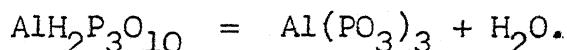
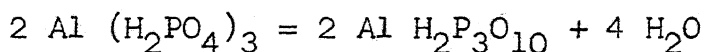


With further reaction with alumina grains in humid condition, hydrated phosphate compounds are produced ;



This phosphate is dehydrated reversibly to $\text{Al} (\text{H}_3\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at 90°C and then decomposed at 150°C into $\text{Al} (\text{H}_2\text{PO}_4)_3$ and AlPO_4 .

Poly- and metaphosphates are formed at $230 - 450^\circ\text{C}$ through condensation reactions from monoaluminium phosphate. The polymer $\text{Al} (\text{PO}_3)_3$ appears at about 500°C , and then condenses to a metaphosphate glassy phase at 1200°C and devitrifies at about 1400°C to cristobalite type AlPO_4 .



Though the above is the general reaction scheme between orthophosphoric acid and alumina, the number and amount of different phases formed at different temperatures may be greatly influenced by different kinetic considerations such as reactivity of the materials concentration, curing time

and temperature, Highly reactive materials such as aluminium hydroxide, transition aluminas and calcined aluminas of high surface area will react quickly even at room temperature. On the other hand, relatively inert materials such as calcined aluminas of low surface area and sintered and fused aluminas will react slowly, and higher curing temperatures would be required to obtain a stable bond, which may be physically and chemically different from the bond developed with more reactive forms of alumina.

The reaction of orthophosphoric acid with alumina occurs at the alumina surface and so the kinetics of the reaction is affected by the total surface area available for the reaction to take place. The fraction of acid reacted at a given temperature and time will increase as the quantity of alumina increases and as the size of individual alumina particles decreases. Commercial powders consist of irregular particles of a wide variety of sizes; hence the specific surface area of the powder, rather than its average particle size is more important.

Figure II-1¹⁸ shows the effect of the specific surface area of the Bayer-process aluminas on the fraction of alumina reacted after 10 days at 150°C. As expected, the quantity of alumina reacted increased with increasing surface area and increasing $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5$ molar ratio (R), but the reason for

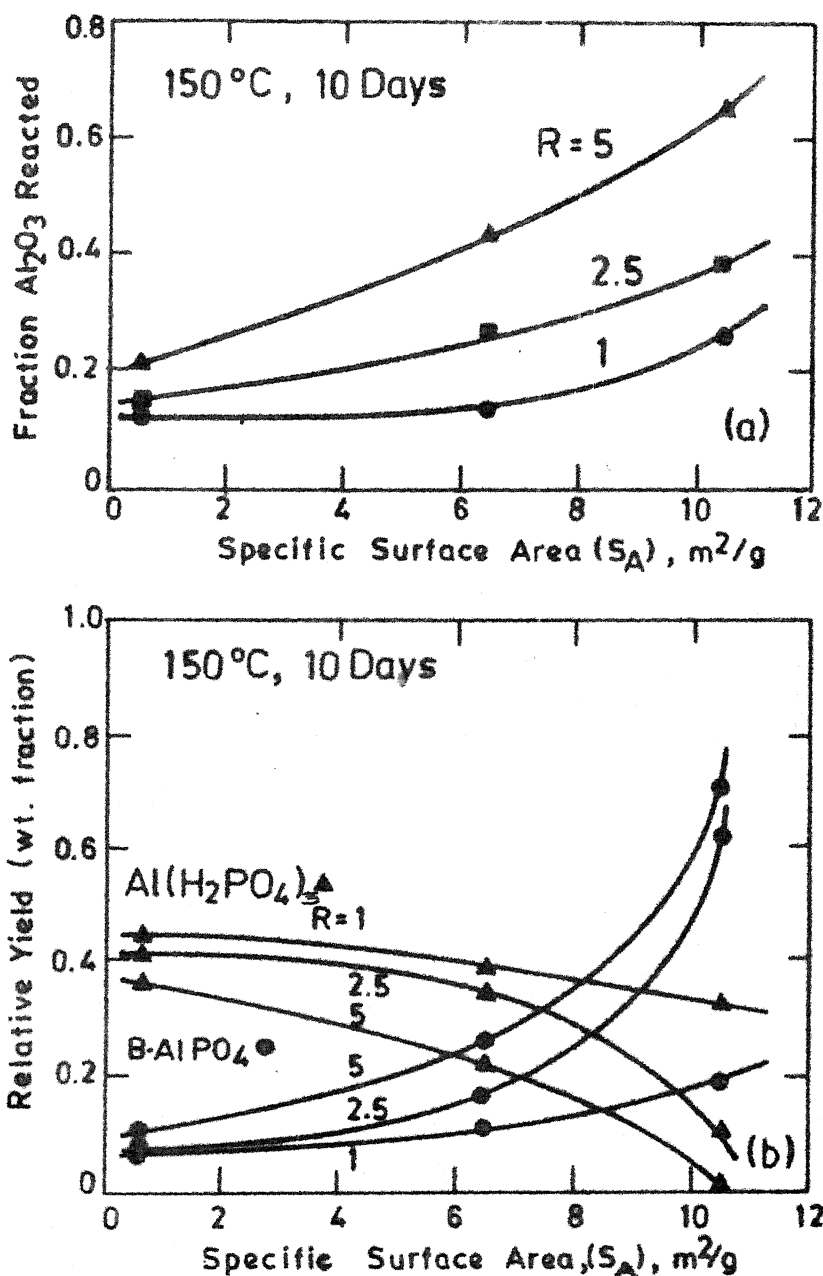


Fig. II-1: Effect of specific surface area and $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ molar ratio (R) on (a) fraction of alumina reacted and (b) yields of $\text{Al}(\text{H}_2\text{PO}_4)_3$ and B-AlPO_4 in mixes of Bayer alumina and orthophosphoric acid reacted 10 days at 150°C .

this increment is not available in literature.

The effect of the specific surface area of the alumina reacted and acid concentration on the yields of $\text{Al}(\text{H}_2\text{PO}_4)_3$ and B-AlPO_4 after reaction at 150°C for 10 days are shown in Figure II-1(B). As can be seen, the relative yield of the acid phosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$ is higher in mixes prepared with aluminas of low specific surface area and low $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ ratio. On the other hand, higher yields of aluminium orthophosphate B-AlPO_4 , are observed in higher surface area mixes or where the $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ ratio is high.

(B) MONOALUMINIUM PHOSPHATE (M.A.P.):

There are some difficulties when phosphoric acid is used directly as bonding agent in that the refractory may bloat during heating owing to the evolution of hydrogen formed by the reaction of the acid with the metallic impurities present in the mixes. To minimise this defect, monoaluminium phosphate is generally used.

A detailed investigation of the $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system shows that with increasing neutralization of H_3PO_4 by Al, the aqueous solution becomes more and more colloidal whereas its stability decreases. Upon heating the phosphates crystallize the more readily the higher is the $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$

ratio, and this occurs at the expense of the bond strength which ideally should be vitreous-amorphous,

The most important characteristic of aluminium acid phosphate binders is the degree of neutralization of the orthophosphoric acid, i.e. the ratio of the mole % of neutralizing oxide and P_2O_5 .

$$N_m = \frac{Me_n O_m}{P_2O_5} \cdot 100$$

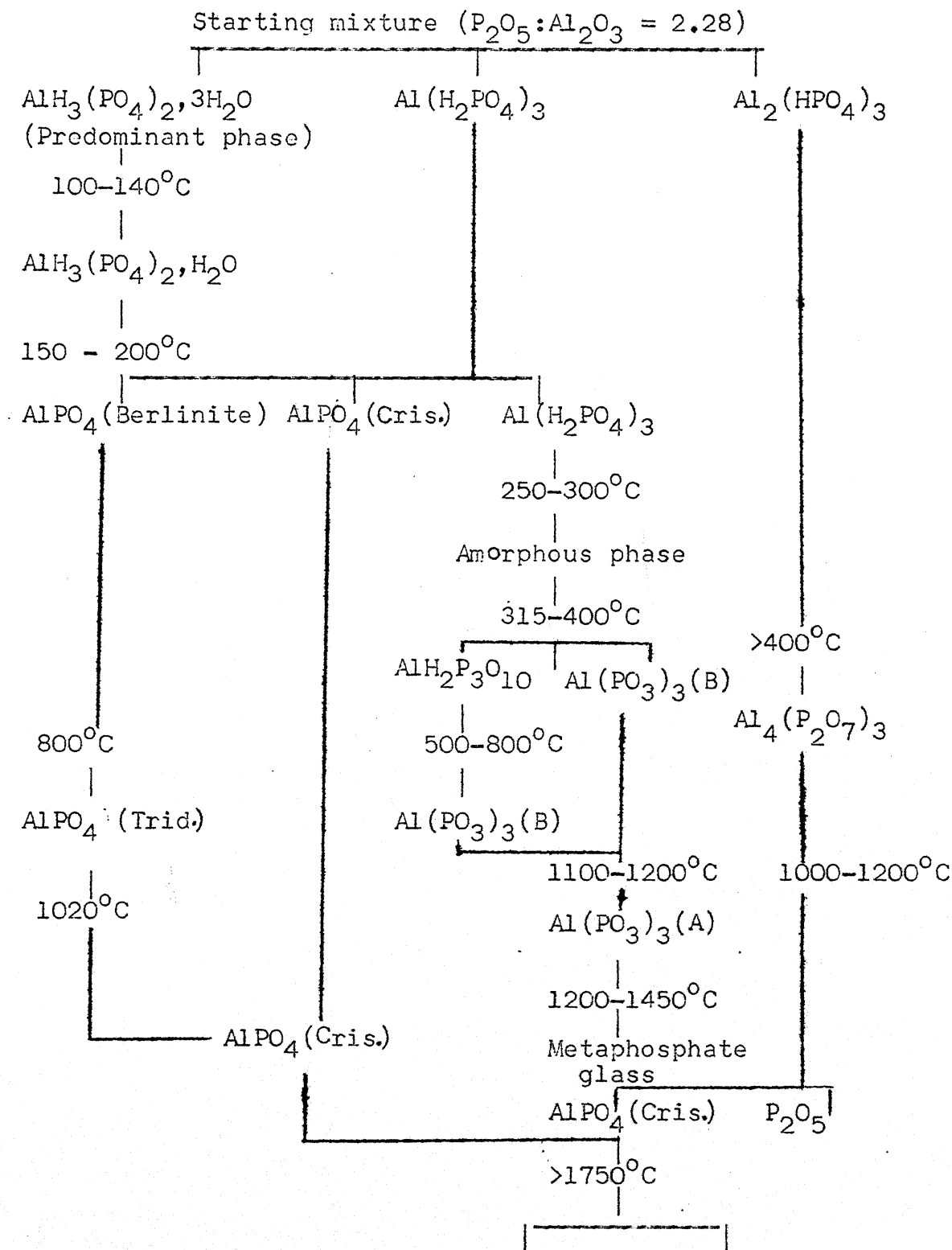
for pure acid $N_m = 0$ for $AlPO_4$ $N_m = 100\%$. The binder properties are best with $N_m = 33-67\%$. Typical commercial²⁰ compositions have $N_m = 33\%$ and are almost 50 wt% solution of $Al(H_2PO_4)_3$.

The P_2O_5/Al_2O_3 molar ratio, x , defined as the acidity of the liquid bond by some authors determines the stability. Thus it has been shown²¹ that mixtures with $x < 3$ are metastable, mixtures in which $x = 2.3$ throw down a deposit and harden on prolonged storage, and mixtures with $x < 2.3$ are even more unstable. Studies of the phase changes that occur when such solutions are heated are numerous. The most detailed studies have been carried out on a binder with $x = 2.28$. The results are summarized in Table II-1¹⁷.

Hydrogen bonded polymers are formed at medium temperature range which then condense to glassy or amorphous

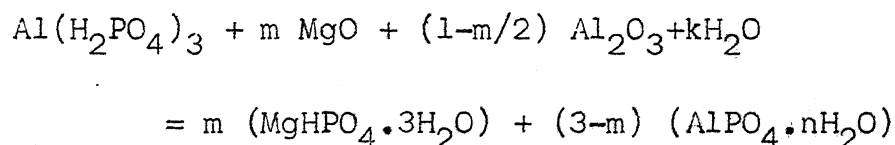
TABLE II-1

Effect of heat treatment on aluminium acid phosphate binder.



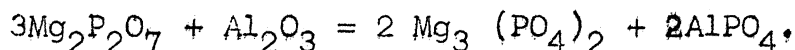
macromolecules at some higher temperature. At still higher temperature, the glassy phase crystallize and the phosphates decomposed thermally.

Cold setting concretes ²² can be prepared by adding a reactive oxide, e.g. MgO. When the molar ratio P: (Al+Mg) is varied, using reagent grade MgO, MAP and Al(OH)₃, the setting rate increases as the amount of MgO is increased. The reaction is endothermic, and the heat of reaction increases with MgO content. The main reaction is represented by :



where m is <2.

Thus crystalline MgHPO₄·3H₂O, as well as AlH₃(PO₄)₂ gel is formed. Attempts to form a cold setting system with P: (Al+Mg) > 1 have failed as a result of the formation of water soluble Mg(H₂PO₄)₂. On subsequent heat treatment, phase changes occur which depend on the ratio P: (Al+Mg). With a ratio of 1.0 the system becomes amorphous as the temperature increases from 200° to 400°C; at > 650°C AlPO₄ (Tridymite) and a small amount of Mg₂P₂O₇ are formed. Above 900°C Mg₃(PO₄)₂ and AlPO₄ (Tridymite) form according to :



There are also indications of solid solution of MgO in AlPO_4 . Concretes based on this system have been patented and are commercially available.

(C) CHROMIUM - ALUMINIUM PHOSPHATE (CAP):

The strength values of refractory bodies can be further enhanced by using chromium phosphate and chromium-aluminium phosphate binders particularly when they are to be heated above 1200°C . The problem associated with the use of MAP only as a bonding agent for high alumina refractories has been highlighted by O'Hara et al ¹⁷. The overall isothermal expansion in refractories bonded with CAP is less than that with MAP indicating less bond decomposition and phase inversions. Again the expansion occurred slowly for CAP indicating that the physicochemical changes in the binder phases are sluggish. Phosphate bonded alumina specimens showed residual expansion after cooling to room temperature, whereas, specimens with CAP showed very little residual shrinkage or no change from original size after heat treatment at 1100°C .

Hence, it is evident that the strength stability of phosphate bonded alumina bodies can be enhanced through the use of chromic acid as partial replacement of phosphoric

acid. Highly colloidal polyorthophosphates can be produced by using Cr_2O_3 beyond the molar proportion of $\text{Al}_2\text{O}_3\text{-}3\text{P}_2\text{O}_5$ upto a proportion approximately corresponding to $\text{Al}_2\text{O}_3\text{ }0.8\text{ } \text{Cr}_2\text{O}_3\text{ }3\text{P}_2\text{O}_5$. These polyorthophosphates behave quite different at elevated temperatures. The tendency of crystallization and volatilization of P_2O_5 are considerably less than in the case of monoaluminium phosphate.

The physicochemical changes produced by the heat treatment of chromium phosphate and chromium-aluminium phosphate have been reported ^{23,24}. Chromium phosphate hexahydrate shows continuous amorphization when heated to 980°C . A metastable low temperature phase, $\beta\text{-CrPO}_4$, is formed and irreversibly inverts to a stable phase $\alpha\text{-CrPO}_4$ at 1200°C . Dehydration of a prepared chromium-phosphate binder with a molar ratio of $\text{P}_2\text{O}_5 / (0.75 \text{ Al}_2\text{O}_3 + 0.25 \text{ Cr}_2\text{O}_3)$ of $= 2.26$ was reported to show a predominantly amorphous phase when heated to 900°C . In these respects these two binders are superior than MAP since they can retain an amorphous phase over a broader temperature range.

Chromium - aluminophosphate binder with various ratios of $\text{P}_2\text{O}_5 / \text{M}_2\text{O}_3$ and $\text{Al}_2\text{O}_3 / \text{Cr}_2\text{O}_3$ are used in industry. Grigorev ²⁵ studied the phase compositions of the thermal transformation products of chromium-aluminophosphate binder with molar ratio $\text{P}_2\text{O}_5 / \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ equal to $1.37 / 0.40 + 0.60$ (composition - I) and $1.67 / 0.56 + 0.44$ (composition -II).

He didn't find any crystalline product when heated to 500°C. At 500 - 800°C, individual fine crystalline formations took place. After firing to 1200°C, the principal phase in compo-I was chromium pyrophosphate $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, with a small amount of $\text{Cr}(\text{PO}_3)_3(\text{C})$ and AlPO_4 (cristobalite). A similar specimen of compo-II, consisted largely of AlPO_4 as cristobalite and $\text{Cr}(\text{PO}_3)_3(\text{C})$ and a very small amount of $\text{Cr}_4(\text{P}_2\text{O}_7)_3$.

The thermo-mechanical properties of phosphate bonded high alumina aggregates were studied by Roy and Sircar²⁶. X-ray analysis of their specimens, in the system $\text{Al}_2\text{O}_3\text{-H}_3\text{PO}_4\text{-CrO}_3$ (where H_3PO_4 had been replaced up to an extent of 30%) after creep test at 1200°C and 1300°C, indicated the presence of $\alpha\text{-Al}_2\text{O}_3$ and AlPO_4 (Cris) only. Such an assemblage implies that chromium oxide has either undergone solid solution with Al_2O_3 or formed a glass of chromium phosphate or aluminium-chromium-phosphate. So, the enhancement of hot strength with CAP could be due to (i) retention of a portion of P_2O_5 in glass state either as aluminium-chromium-phosphate or chromium phosphate, and (ii) reinforcement of partly crystalline aluminium phosphate with either aluminium-chromium phosphate glass or chromium phosphate glass which resists the flow of bond.

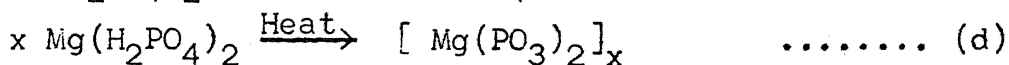
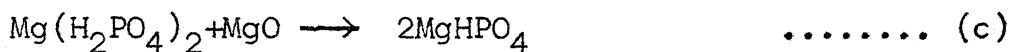
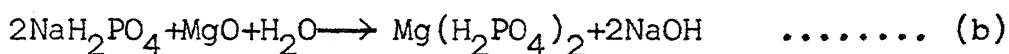
(D) ALKALI POLYMETAPHOSPHATES :

The reaction between magnesia and phosphoric acid or acid phosphates is usually quiet violent and therefore not satisfactory for commercial basic brick manufacture. Much work has however been done for the development of phosphate bonded dry basic ramming mixes where a rapid set and bond development is desirable. Yount ²⁷ mentions complex polyphosphates as chemical bonds in basic gunning mixes for electric and basic oxygen furnaces.

The use of alkali metaphosphates as a bond for refractory mortars was first investigated by Herold and Burst ²⁸. Sodium hexametaphosphate $(\text{NaPO}_3)_6$, forms rubber like polymers and yields high strength mortars with fireclay aggregates. These materials are used in high alumina refractory mortars and ramming mixes, and are particularly useful as bonds for basic aggregates as recognised by Limes and Russell ²⁹. These authors studied the effect of chain length (\bar{n}) on cold and hot strengths of basic compositions and found $\bar{n} = 20$ is optimum. Bonding of basic refractories with sodium polyphosphate bonds was studied by Lyon et al ³⁰.

heating curing process. On degradation, the acid component reacts with MgO to produce the bond. Salts that are not degraded or are not soluble do not give the desired bond strength.

Salts that contain any acidic hydrogen atoms react very rapidly and produce a hard unworkable mass much like that produced by orthophosphoric acid. In the presence of sufficient amount of bond, the following reactions can occur to form a strong body:



From the chemical and X-ray diffraction results, it is suggested that the bonding of MgO between 200-1200°C is caused by amorphous phosphate glasses formed by the above reactions. As the temperature approaches 1300°C, the bond becomes more crystalline with the formation of magnesium orthophosphate or farringtonite ($3\text{MgO} \cdot \text{P}_2\text{O}_5$). This increase in crystallinity is accompanied by a loss of strength indicating that $\text{Mg}_3(\text{PO}_4)_2$ is not a bonding agent.

Foessel and Treffner³¹ studied the use of sodium polyphosphates in basic refractories. Since relatively 'inert' glassy polyphosphates were used in the majority of the earlier experimental mixes, another binder such as chromate, sulphate, sodium silicate or hydraulic cement had to be added to impart the 'rapid set' desirable in such applications. He used such double bond forming additions with glassy sodium polyphosphates of chain length 21. He also found out the criteria $\text{CaO} : (\text{P}_2\text{O}_5 + \text{SiO}_2)$ ratio is important for the strength values of the basic bricks.

The individual reactions of sodium polyphosphates with magnesia, calcia and a mixture of them, in presence of silica was reported by Venable and Treffner³²

(i) They identified $\text{Mg}_3(\text{PO}_4)_2$ as the only crystalline phase by the reaction of magnesia and sodium polyphosphate when heated to 1720°C .

(ii) With lime at 800°C the product formed is sodium calcium orthophosphate ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot \text{P}_2\text{O}_5$). This compound remained unchanged as the firing temperature was increased but began to decompose with volatilization of sodium at 1500°C . The high temperature phase remaining was whitlockite ($3\text{CaO} \cdot \text{P}_2\text{O}_5$, calcium orthophosphate).

(iii) In mixtures of magnesia, calcia and sodium phosphate polymers, the same sodium calcium phosphate was formed starting at 800°C . Magnesia did not react until soda began to volatilise at 1500°C . Above this temperature magnesia entered the whitlockite structure in relatively small amounts.

(iv) In presence of silica, calcium silico-phosphate (e.g. nagelschmidtite solid solutions) formed at the expense sodium calcium bonding phases which was detrimental for phosphate bonded basic refractories.

(v) The principal phosphate containing bonding phases in 50-90% MgO class refractories with 5% glassy phosphate and 3% of a lime-containing binder which form active CaO on decomposition at $300-900^{\circ}\text{C}$ are as follows. Complex sodium phosphates below 800°C , these change to sodium dicalcium phosphate (solid soln.) at $800-1500^{\circ}\text{C}$, and to calcium orthophosphates at higher temperature. These changes are irreversible but appear to be of such a nature that the continuity of a strong bond is maintained over the entire temperature range.

(E) ALUMINIUM CHLOROPHOSPHATE HYDRATE:

Aluminium chlorophosphate hydrate, a dry powder, was developed especially for use in castable

refractories and to overcome the problems associated with bond migration, bloating caused by metallic iron and the instability of some refractories on storage. It is highly soluble in water, and decomposes on heating to form AlPO_4 without forming intermediate metaphosphates. It can be used in both heat setting and cold setting compositions (the latter by the addition of MgO). The recently modified binder includes a small proportion of an acetylenic alcohol condensate that permits its use in conjunction with aggregates containing metallic Fe. The alcohol retards the reaction between HCl and Fe, and minimizes bloating. The thermochemistry of aluminium chlorophosphate hydrate makes possible rapid heating without cracking or spalling of the refractories.

(F) AMMONIUM PHOSPHATE:

To minimize the rate of reaction between magnesia and phosphoric acid the latter can be successfully replaced by ammonium phosphate . A complex ammonium phosphate solution, sold principally to the fertilizer industry as Sequestered Phosphatic Solution (SPS) , can be used as a bond as reported by Limes ³³. It is a mixture of ortho, pyro and poly ammonium phosphates in which a very high percentage of P_2O_5 is in solution. In contrast to phosphoric acid, SPS reacts slowly with magnesia but still produces a hard refractory body. The degree of dead burning of magnesia

aggregate, its fineness and the temperature at which the mixture is made influence the rate of setting. The three distinct advantages are improved hot strength, ability to build up heavy sections on cold gunning and better adherence of the phosphate bonded materials to slagged surfaces. But the disadvantages are : One , evolution of ammonia gas and two, extremely rigid structure which makes the drying of the refractory difficult.

(G) OTHER PHOSPHATE BONDS:

When powdered alumina-lime- silica glass is mixed with phosphoric acid, it forms a hard white translucent mass. It is seen that 30% of the powder goes into solution and the mixture sets with the formation of a silica gel. Various auxiliary materials may be added to alter the properties of this, but the basic setting mechanism is the formation of a silica gel structure somewhat on the line of setting of soluble silicate bonds.

Many suggestions have been made regarding the use of phosphoric acid with siliceous materials in refractories. Thus bonding depends on the solution of silica by phosphoric acid and on the formation of a silica gel structure. It has been suggested that in the heat setting processes silyl metaphosphate, $\text{SiO}(\text{PO}_3)_2$, is formed at temperature higher than 260°C .

The use of phosphates as bonds for unfired silica bricks was first reported by Kainaraskii ³⁴, but it was not very popular due, to the higher cost of the phosphate bond and also the unfired silica bricks with phosphate bonds are very hygroscopic and difficult to store.

Mitra et al ³⁵ have tried phosphate bonds to make unfired silica bricks. The bond development took place around 300°C due to the interaction between SiO_2 and P_2O_5 with the formation of $\text{SiO}(\text{PO}_3)_2$. But the strength values of the samples are not very high even after heat treatment which may be due to the fact that the samples were made from the waste silica product during the dismantling of coke ovens, and hence the silica grains were in an inactive state.

Possible improvement of silica brick by using AlPO_4 as a mineraliser and bonding material appears rather plausible from the view point of crystal chemistry and isostructural relations ³⁶. Considerable acceleration of the inversion of quartz to cristobalite can be observed by the addition of AlPO_4 , along with an increase in refractoriness of the brick. There are no crystalline solution between silica and AlPO_4 in their cristobalite type modification. Whereas SiO_2 (cristobalite) shows inversion anomalies as

a function of thermal history of the samples, AlPO_4 (cristobalite) is free from such phenomenon (inversion point $\alpha \rightarrow \beta$ at about 185°C).

Sometimes, a combination of different phosphate bonds are used to enhance the bonding properties. Mix binders comprising aluminium phosphate and ammonium or urea phosphate have been developed for use in heat setting high alumina compositions where a dry powder bond is required.

Different acid phosphate bonds are also added along with phosphoric acid. It is seen that the cations which are weakly basic or amphoteric in nature and which have moderately small atomic radii, are required to increase the bonding power. Thus addition of aluminium, beryllium, ferric or magnesium phosphates increase the strength of the bond. In contrast, additions of calcium, barium and thorium decreases the effectiveness of phosphoric acid as a bonding material. All these cations are either highly basic or have large ionic radii.

3. PROPERTIES OF PHOSPHATE BONDED REFRACTORIES

(A) HIGH ALUMINA REFRACTORY:

High alumina refractories are by far the main field of study of different phosphate bonds. Pressed

brick composed of high alumina aggregates containing 5 to 10 wt% of the phosphate bond need only to be cured at moderate temperatures. These products have high cold crushing strengths, accurate dimensions and good slag and abrasion resistance properties that have made them acceptable for use in electric arc furnace roofs.

Palfreyman³⁷ compared the properties of a variety of high alumina brick bonded with H_3PO_4 with those of similar products bonded with calcined Al_2O_3 and calcined $Al_2O_3 + SiO_2$ mixtures (Fig.II-2). The phosphate bonded product shows good strength at moderate temperatures but a lower strength than the others above $1300^{\circ}C$.

Jackson and Partridge⁵ compared the properties of various types of bricks (including the phosphate bonded high alumina type) for electric arc furnace roofs. The phosphate bonded product has properties similar to those of the fired brick not containing phosphate, but had only 1/3 the hot MOR and failed in torsion at $1300^{\circ}C$. These workers observed that in some furnaces , these properties may impart slag resistance superior to that of the ceramic-bonded product. However, the addition of P_2O_5 reduced the refractoriness of the 80-85% Al_2O_3 bodies.

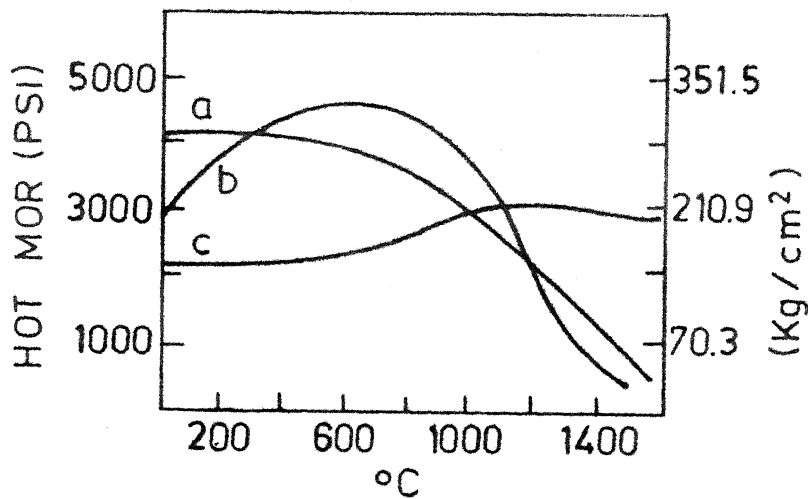


Fig. II.2: Hot MOR of refractory bodies with tabular Al_2O_3 base, fired at 1700°C and bonded with (a) calcined Al_2O_3 , (b) calcined $\text{Al}_2\text{O}_3 + \text{H}_3\text{PO}_4$ and (c) calcined $\text{Al}_2\text{O}_3 + \text{SiO}_2$.

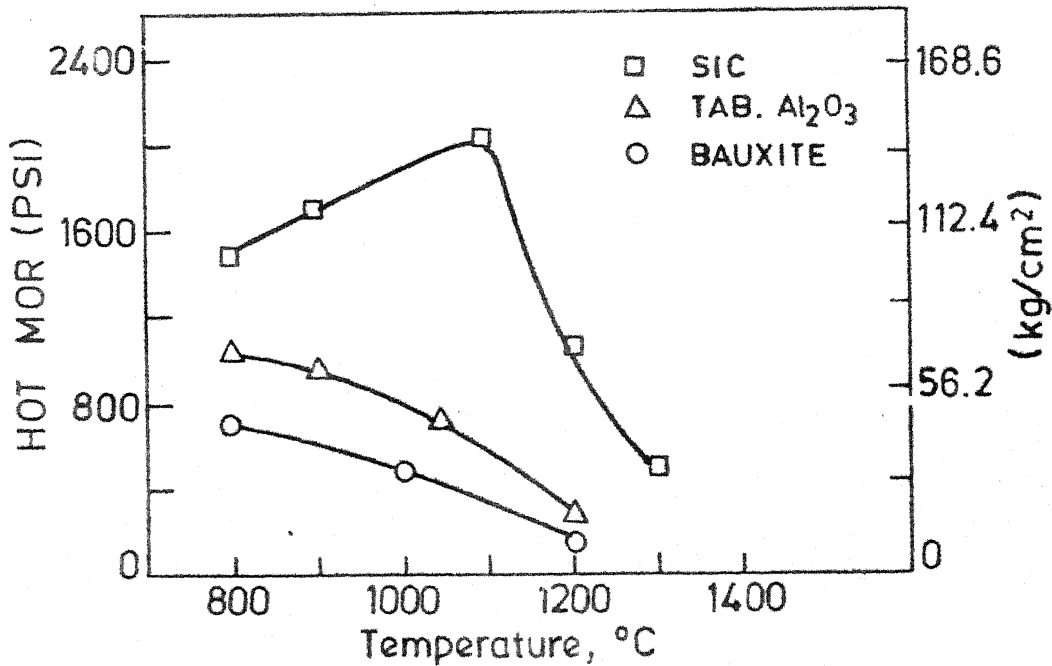


Fig. II-3: Hot MOR of phosphate-bonded castables.

Fisher³⁸ studied the bonding of alumina powder by a number of phosphate bonds and also aluminium mono-acetate and ethyl silicate bonds. The porosity, cold crushing strength and transverse breaking strength values of the pressed alumina-bond samples fired upto 1400°C showed that the phosphates are the strongest and the strength increases with increasing acidity. Cold crushing strength upto 55000 lb/in² can be obtained with chromium-aluminium phosphate bond and open porosity up to 13% can be achieved by the same when fired up to 1400°C. It was concluded that it is possible to fabricate strong, relatively dense (80-85% theoretical density) ceramic articles to close tolerances, with good dimensional stability upto 1000°C.

Roy and Sircar²⁶ compared the cold crushing strength and RUL values of high alumina ramming mass samples bonded with mono-aluminium phosphate and chromium-aluminium-phosphate. The CCS values using 12% of the bond may be as high as 1380 Kg/cm² for CAP and 1260 Kg/cm² MAP when fired at 1600°C. The RUL values are also higher for CAP. ($T_a=1410^\circ\text{C}$ with 7% CAP cured at 500°C).

Phosphate bonded high alumina refractories are often described as having good slag resistance. In the case of refractories bonded with MAP, the composition of the slag

is most important ³⁹. Thus, Na_2O , K_2O and PbO react with AlPO_4 at temperatures above 800°C ; CuO and CaO react above 1400°C . Menjscikov et al ⁴⁰ have shown that $\text{Al}_2\text{O}_3 + \text{H}_3\text{PO}_4$ ramming compositions are particularly resistant toward Fe_2O_4 slags at temperatures up to 1350°C . Moreover slagging occurs only when 2% MgO is present.

Resistance of the phosphate bonded refractories to metal infiltration was studied by Feldhus ⁴¹. It has been shown that the addition of P_2O_5 reduces the surface energy of the refractory so that it is poorly wetted by molten metals and slags.

Cement free phosphate-bonded high alumina castables are available either in one pack systems based on solid phosphate bonds (e.g. aluminium chlorophosphate hydrate) or two pack systems containing liquid bonds (e.g. MAP). These materials set in the cold by the reaction of the acid bond with MgO ; their properties vary depending on the type and amount of the bond used and the type and grading of the aggregates. Typical hot MOR values for SiC , Al_2O_3 and bauxite castables bonded with aluminium chlorophosphate hydrate are shown in Fig. II-3.

Tabular alumina based castables show a reduction in hot strength above 800°C . This decrease is

more severe for materials containing MgO as a setting agent. This type of castable, however is used widely in chemical plants and has been shown to be very effective in electric arc furnace roof. The maximum MOR for SiC is at 1100°C which is thought to result from formation of silico-phosphates. The addition of SiC to high alumina phosphate bonded products causes a definite increase in hot strength,

(B) BASIC REFRACTORIES:

Sodium polyphosphate, ammonium phosphates are the main phosphate bonds used in basic refractories. Fossell et al ³¹ worked on magnesite compositions and used glassy phosphates as the binding agent. Even with 5% only of the bond, better strength value can be obtained. Fig. II-4 shows the hot MOR of a typical product bonded with sodium polyphosphate.

Chemically bonded bricks show the normal trend of high strength at low temperature which gradually and progressively diminishes and is not regained until $1100-1200^{\circ}\text{C}$ when the ceramic bond develops. The high fired direct bonded Mg-Cr brick exhibits a gradual but persistent strength increases from $800-1200^{\circ}\text{C}$ by tightening its structure, thereafter, strength decreases due to expansion reactions and associated grain boundary slip. The burnt periclase and phosphate

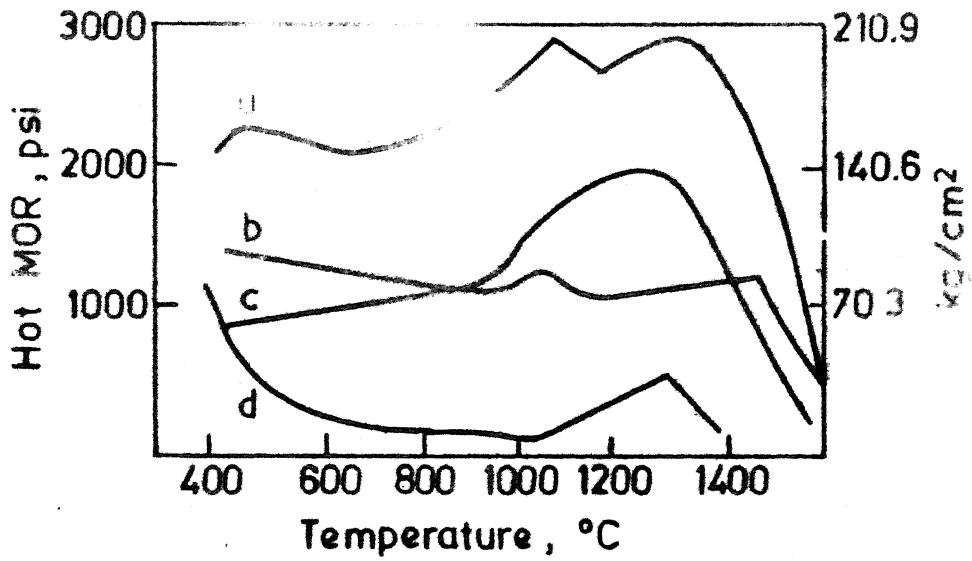


Fig. II-4: Hot MOR of basic refractory bricks. (a) Phosphate bonded. (b) burned paricalse. (c) direct bonded Mg-Cr and (d) Chemically-bonded Mg-Cr.

bonded magnesite composition have similar temperature coefficient of strength as both are relatively constant over the same temp. range upto 1500°C ; however the strength level of phosphate-bonded composition is at least twice that of burnt periclase type upto 1600°C . There is evidence (as may be expected) that failure of the phosphate bonded brick is more of viscoelastic (plastic flow) type than the brittle fracture prevalent for the burnt periclase brick.

The authors have also studied the effect of glassy phosphate additions on mag-chrome compositions and they found that except for porosity, phosphate bonding was superior to conventional bonding in all properties determined. Bulk densities are measurably increased and improvement in cold strengths are outstanding and equally good are the hot load properties.

Within the phosphate bonded group of mixes, increased chrome ore content results in the expected increase in brick densities . Porosities after 1100°C are fairly constant. Hot MOR at 1200°C are very high but appear to decrease somewhat with increasing chrome ore content. Deformations under compressive load at 1700°C are generally low and in lower MgO brick a marked pyroplasticity allows an exceptionally large deformation without shearing. The pyroplastic character of phosphate bonded brick is also displayed under

hot transverse load conditions where permanent bending without failure is observed ⁴².

Lyon et al ³⁰ studied the effect of chain length (\bar{n}) of the sodium polyphosphate bond on the strength properties of high purity magnesite refractory (96 - 98% MgO) using 3-6% of the phosphate binder and about 4-5% water. As chain length increased, the cold modulus of rupture also increased. Glassy phosphate of shortest chain length (6-8) exhibited highest hot MOR value but lowest cold MOR value. They also reported that the rate of reaction between magnesia and phosphate decreased with increasing chain length.

The effect of amount of bond on the strength values was also examined by them. As the amount of bond increased, cold modulus increased, as the amount of bond decreased, the hot strength increased until 2.25% bond was reached, amounts below this level poor results were obtained.

Gilham-Dayton ⁴³ tested ammonium phosphates $[(\text{NH}_4)\text{H}_2\text{PO}_4, (\text{NH}_4)_2\text{HPO}_4]$ in chrome-mag and magnesite refractories. In all the cases, the chemical bond strength remains high until a ceramic bond is formed. Although the overall strength decreases in the range at 1000 - 1250°C.

He used ball clay along with the phosphate bond in some cases and found that ball clay also contributes to the bond strength at lower-medium temperatures (up to 1000°C) but at higher temperature ($1300 - 1500^{\circ}\text{C}$) the samples bonded without clay are better.

(C) OTHER REFRACTORIES:

Gilham-Dayton ⁴³ tested silica fines with phosphoric acid (sp.gr. 1.75) and monoaluminium phosphate solution (48%) in amounts of 11% and 12% respectively. After firing the samples in the temperature range $400-1500^{\circ}\text{C}$, it was found that the highest strengths for both the cases are obtained at 1100°C and the samples bonded with phosphoric acid were much stronger (CCSvalue = $9700 \text{ lb}_f/\text{in}^2$).

The results were entirely reverse for synthetic mullite grog . He used monoaluminium phosphate (5.8%) for one group, and clay (4%) plus H_3PO_4 (2.5%) for another, with 1-4% water for pressing the samples. For all the cases, monoaluminium phosphate samples were better and the strength increased in both the cases with firing temperature.

Very little literature is available on phosphate bonding of SiC. Karklit et al ⁷ studied the effect of different phosphate bonds on the cold strength, hot strength and

porosity values of SiC gunite compositions. For the samples bonded with sodium tripolyphosphate and clay in different proportions, the CCS value was highest (600 Kg/cm²) with 25% clay and 6.7% phosphate. With sodium tripolyphosphate alone, best results were obtained with 5% of the bond.

He also used 10% each phosphoric acid and monoaluminium phosphate. The CCS value as well as porosity was better with phosphoric acid bond (CCS = 760 Kg/cm² and porosity 17.8% when fired at 1200°C).

The comparative study of the SiC samples bonded with these three phosphate bonds showed that H₃PO₄ was the best bond.

CHAPTER -III

OBJECT OF THE PRESENT WORK

Silicon carbide is an important industrial material. It is used in the manufacture of electric heating elements, grinding wheels and rubbing stone, and as a refractory specially for high temperature heat exchangers and abrasion material. Due to the strong covalent bonding between silicon and carbon, silicon carbide is a very difficult material to sinter. In order to achieve sintering at reasonable temperatures it is necessary to incorporate bonds such as clay (clay-silicon carbide refractory) or glassy frits (grinding wheels). But, not only the refractory properties of silicon carbide are significantly degraded, but the sintering temperatures are still quite high, 1200 - 1600°C, depending on the amount and nature of bond used. Also, firing rejects due to deformation, slumping and dimensional inaccuracy, specially for intricate and large pieces, can be very high. Phosphate bonded silicon carbide could provide an attractive alternative fabrication route for some applications, e.g., large structure heat exchangers, low temperature fired rubbing stones, abrasion resistance liners for hydrocycloner, ash discharge gate etc.

The aim of this work is to find a suitable phosphate chemical bond and a bonding matrix for silicon carbide in order to achieve the necessary strength at a lower firing temperature. The programme details are as follows:

- (a) Preparation of different phosphate bonds,
- (b) Selection of the optimal combination of bond and bonding powder matrix for silicon carbide,
- (c) Determination of optimal process parameters, moulding pressure and curing temperature for phosphate bonded silicon carbide,
- (d) Determination of different kinds of properties of phosphate bonded silicon carbide.

CHAPTER - IV

MATERIALS AND METHODS

1. MATERIALS

The materials used in this study were silicon carbide, fly ash, thermit slag, china clay, rice husk ash, window glass, pyrex glass, talc, alumina and different chemicals.

(A) SILICON CARBIDE:

Silicon carbide (SiC) or carborundum is an entirely synthetic material produced in electric resistance furnace from mixture of pure quartz sand, petroleum coke, 5-10% fine sawdust and 1-2% NaCl at a temperature of about 2200°C. It has two crystalline modifications; the low temperature β - SiC has cubic structure with diamond type lattice and the high temperature α - SiC has a hexgonal crystal lattice. The mineral dissociates to silicon and carbon without passing through a liquid phase at 2700°C.

Density of commercial SiC is 3.21 gm/cc, Mohs hardness is 9.5 - 9.75, thermal conductivity is high (0.04-0.49 cal/sec, cm, °C at 600°C) and co-efficient of expansion is very low.

The different batches of silicon carbide used in this study are given in Table IV-1:

Table IV -1

Gradings for different batches of silicon carbide

Batch No.	Silicon Carbide%					
	Grit No.	7/12	14/30	36/70	100	200/270 270/400*
	Size in mm.	2.8/1.7	1.4/0.6	.425/.212	.15	.075/.053 .053/.037
1	-	55	10	10	10	15
2	-	-	26	74	-	-
3	-	40	44	16	-	-
4	45	40	-	15	-	-

* Coded as 3F and C.

(B) FLY ASH:

Pulverised fuel ash (PFA) or fly ash, is an industrial waste product obtained in huge quantities from flue gases of thermal power stations using pulverized coal as fuel. Mineralogically, magnetite, hematite and glass contaminated with different amounts of unburnt carbon are its main constituents. The amount of glassy phase and

unburnt carbon influence the properties of fly ash,

The fly ash was obtained from the Panki thermal power station. The properties of this fly ash were ⁴⁴:

Chemical analysis (wt%):-

SiO_2 - 57.1, Al_2O_3 -33.1, Fe_2O_3 -5.2, CaO -2.3,

S - 0.12, LOI - 3.0.

Physical characteristics:-

Blain surface area (cm^2/gm)- 4914

Apparent density (gm/cc) - 2.26

Bulk density (gm/cc) - 0.94

(C) THERMIT SLAG:

Thermit slag is produced in the manufacture of ferroalloys by reduction of FeO mixed with chrome ore, manganese ore, tungsten ore etc., in the presence of CaO ; aluminium powder provides the heat for the fusion of the mass by reduction of oxide ores. The typical analysis of the slag is given⁴⁵:

Chemical analysis(wt%):

SiO_2 - 2.10, FeO -0.16, Al_2O_3 -80.30, CaO -6.0, MgO -0.9, MnO -10.1.

The high amount of Al_2O_3 in it leads to refractoriness values of above 1650°C and being a cheap waste product it is of considerable interest to the technologists.

The thermit slag was obtained in the form of large lumps and after size reduction and fine grinding the physical characteristics of the slag powder as determined by earlier workers are ⁴⁵:

Blain surface area (cm^2/gm) - 2900

True density (gm/cc) - 3.397

Bulk density (loose) (gm/cc) - 1.126

Bulk density (tap) (gm/cc) - 1.40

(D) CHINA CLAY:

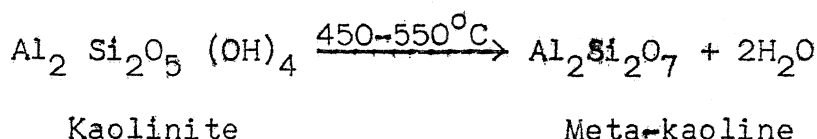
China clay is a residual clay, comprised primarily of kaolinite minerals. It is widely available in nature but is seldom pure. The chemical composition lies in the range :

SiO_2 - 45 - 50%, Al_2O_3 - 30-40%, $\text{K}_2\text{O} + \text{Na}_2\text{O}$ - 2-3%, Fe_2O_3 - 0.5-2.5%,
 $\text{CaO} + \text{MgO} + \text{MnO}$ - 0.5 - 1.5%, LOI - 12-13%.

It is known that at around 800°C all weight loss is complete and the clay acquires its maximum pozzolanic activity due to amorphous or highly distorted phases present. It was felt that phosphate reactions with clay, calcined at 800°C , should be most suitable.

Following changes occur in raw china clay when it is heated ⁴⁶:

Upto 350-400°C, only the physically adsorbed water is given up. At 450-550°C, the kaolinite structure breaks down due to an endothermic dehydroxylation reaction with a loss of weight of about 14% and the formation of metakaoline phase.



Hence the clay used in this study was calcined to 800°C for 3 hrs. in lump forms and then ground in ball mill for 30 hrs. to get fine calcined clay powders.

(E) RICE HUSK ASH:

Rice husk ash is the combustion product of rice husk, an agricultural waste material. It contains upto 97% SiO₂. Depending on the time and temperature of combustion and the impurities present the silica in the ash remains either in an amorphous phase or is transformed into its various polymorphic modifications-quartz, tridymite and cristobalite. The refractoriness of rice husk ash is normally about 1600°C. It is a highly porous, light-weight and bulky material. The chemical composition

of rice husk ash is :

Chemical analysis (wt%):⁴⁵:-

SiO₂-87-97 , CaO 0.2 -1.5 , MgO 0.1-1.95 , K₂O 0.6-2.5 ,
Na₂O - trace -1.75 , Fe₂O₃ - trace- 0.55 , P₂O₅- 0.2-2.8

The ash used in this experiment was prepared by burning rice husk in the laboratory in TIB (Tube-In-Basket) furnace. Due to low temperature of burning, this ash had amorphous silica with bulk density (loose) of 0.098 gm/cc and tap bulk density of 0.25 gm/cc.

(F) WINDOW GLASS:

Window glass belongs to the Na₂O-CaO-SiO₂ system having the following typical physical and chemical properties:

Chemical analysis(wt%) :-

SiO₂- 72.7, CaO - 8.4, Na₂O - 13.1, K₂O-0.5, Al₂O₃-1.1.

Density = 2.46 gms /cc, Strain point = 505°C,

Annealing point = 548°C , Softening point = 730°C.

The window glass powders used in this study was fine ground in a ball mill for 48 hours.

(G) PYREX GLASS:

Pyrex glass falls under the borosilicate glass family. It has a low thermal expansion and good resistance

to thermal shock. The typical physical and chemical characteristics are:

Chemical analysis (wt%):-

SiO_2 - 80.3, B_2O_3 -12.3, Na_2O -4, K_2O -0.4, Al_2O_3 -2.3

Density - 2.42 gm/cc, Strain point - 520°C ,

Annealing point- 545°C , Softening point- 734°C ,

The pyrex glass used was in very fine powder form.

(H) TALC:

Structurally, Talc is a hydrated alumino silicate of the formula $\text{Mg}_3 \text{Si}_4\text{O}_{10} (\text{OH})_2$. It cleaves easily along one plane, soft and has a characteristic soapy feel.

Typical properties of Indian Talc are⁴⁷:

Chemical analysis (wt%):-

SiO_2 -61.24, MgO - 32.42, Al_2O_3 -1.42, Fe_2O_3 -0.02, LOI-4.90.

Vitrification range: 1270 - 1350°C , Melting point: 1490°C ,

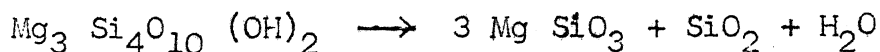
Specific gravity : 2.6 - 2.8, Hardness : 1-2 Moh.

Following changes occur when raw talc is heated^{46,47},

The physically adsorbed water comes off in stages at 120 - 200°C and 350 - 550°C , the weight loss being about 0.4%.

The chemically bound hydroxyl group comes off at 600 - 900°C ,

when some free silica also splits off leaving behind magnesium metasilicate. The weight at this stage is about 5.1% less .



Both raw and calcined talc were used in this study. The calcination was done at 900°C for 3 hours to get it dehydroxylized. No grinding was necessary since it was in very fine powder form.

(I) ALUMINA :

α - Al_2O_3 , also known as corundum , is the common form of alumina and also the most stable. Commercially it is made by Bayer's process from bauxite. High grade commercial alumina contains 0.1-0.2% Na_2O , 0.1% CaO and traces of Fe_2O_3 , TiO_2 , Cr_2O_3 as impurities. Fused corundum is a white, very hard crystalline substance. Its specific gravity is about 3.9 and melting point is 2050°C.

The fused alumina used in this study was supplied by M/S Orient Abrasive Ltd.,. It was ground wet in a ball mill for 60 hrs. and then oven dried to get fine alumina powders.

(J) CHEMICALS:

The following chemicals were used in this study:

(i) Orthophosphoric acid (88-93%), H_3PO_4 .

Mol. wt. = 98.00.

Density at 20°C = 1.75 gms/cc.

(ii) Di-ammonium hydrogen orthophosphate.

$(\text{NH}_4)_2 \text{HPO}_4$.

Mol. wt. = 132.06.

(iii) Aluminium ammonium sulphate.

$\text{Al NH}_4.(\text{SO}_4)_2. 12\text{H}_2\text{O}$.

Mol. wt. = 453.33.

(iv) Sodium hexametaphosphate $(\text{NaPO}_3)_6$.

(v) Chromium trioxide (CrO_3):

Mol wt = 100.01.

? METHODS:(A) GRINDING: -

Grinding was done in ceramic jars of height 21 cm and internal diameter 28.5 cm. The grinding media was alumina cylinders of height 2.072 cm and diameter 2.065cm. The ball mill rpm was 60.

Bayer's alumina was ground wet and the weight ratio of alumina: water : grinding media was 1:1:3. The total amount was fixed so as to fill up 60% of the jar volume. The precalcined china clay was ground dry and the weight ratio of clay: grinding media is 1: 3.

(B) PREPARATION OF PHOSPHATE BONDS:

Monoaluminium phosphate and chromium aluminium phosphate were prepared from L.R. grade chemicals. Three types of alumina were used for this purpose:

- (a) Ground Bayer's alumina,
- (b) Pure fused alumina and
- (c) Alumina derived from thermal decomposition of aluminium ammonium silphate.

To get alumina from aluminium ammonium sulphate, the latter was calcined to a temperature of 900°C for 3 hrs. 12 molecules of hydration water, come off at about 250°C to give porous, dry ammonium alum $[\text{NH}_4.\text{Al}(\text{SO}_4)_2]$. Decomposition of the anhydrous material begins at 280°C and pure $\gamma\text{-Al}_2\text{O}_3$ of very high surface area and reactivity is formed at about $850\text{--}900^{\circ}\text{C}$.

The composition of the bonds and proportion of chemicals for the preparation of such bonds are given in Table -IV-2 and Table IV-3.

Table IV-2

Chemical composition of bonds (wt%)

Constituents	MAP	CAP(I)	CAP(II)	CAP(III)
Al_2O_3	13.6	13.0	12.3	11.9
P_2O_5	56.9	54.3	52.0	49.8
H_2O	29.5	28.1	27.0	25.8
Cr_2O_3	-	4.6	8.7	12.5
Molar Ratio				
$\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 :$	1:3:0	1:3:0.25	1:3:0.50	1:3:0.75
Cr_2O_3				

Table IV-3

Proportion of chemicals for the preparation of bonds (gm)

Chemicals	MAP	CAP(I)	CAP(II)	CAP(III)
Al_2O_3	46.5	43.5	43.5	43.5
H_3PO_4	296	278	278	278
CrO_3	-	20	40	60

The chemicals were taken in 1000 cc conical flasks, which were kept in an oven for 10 days at 150°C. The level of the liquid in the conical flask was maintained by adding distilled water from time to time.

(C) PREPARATION OF TEST SAMPLES:

(i) MIXING:-

Different amounts of silicon carbide grits were mixed with the liquid bond in mortar-pestle thoroughly to get a uniform mix. The time of mixing was about 15 minutes. The mixing of thermit slag and phosphoric acid had to be done quickly so as to prevent premature and localized setting of the mixture.

(ii) PRESSING:-

The green moist mix was pressed in the steel die under a hydraulic press (made by Associated Instruments Manufacturers India Pvt. Ltd.). The pressed samples were then stripped out of the mould carefully.

(iii) DRYING :-

The pressed samples were dried in an air oven for 18-30 hours at a temperature of 100-120°C.

(iv) FIRING:-

Curing was done in an electrically heated automatically controlled furnace at four different temperatures;

400°C, 600°C, 800°C and 1000°C. The time of soaking for each temperature was 5 hours. The time taken to reach the final temperature in each case was follows:

- 400°C - 2 hours .
- 600°C - $2\frac{1}{2}$ hours.
- 800°C - 3 hours.
- 1000°C - 4 hours.

After firing, the samples were cooled overnight inside the furnace.

(D) TESTING OF THE SAMPLES:

(i) BULK DENSITY:-

The weight of the sample was taken and the volume was determined by measuring the radius and the thickness of the sample. The bulk density was computed by using the following relationship:

$$\text{Bulk density} = \frac{W}{\pi r^2 \times t} \quad \text{gms/cc}$$

where,

W = Weight of the sample, gms .

r = Radius of the sample, cm .

t = Thickness of the sample, cm.

(ii) SPLITTING TEST (BRAZILIAN TEST):

The cylindrical pellets were placed such that their axes were horizontal to the platens of the testing machine and the compression load was applied on the curved surface. The failure occurs by splitting the sample along the vertical diameter. The final load to fracture was used in the following relationship to obtain the value of the tensile strength of the sample.

$$\text{Tensile strength} = \frac{2P}{\pi t D} \text{ Kg/ cm}^2$$

where

P = Load of fracture, Kg.

t = Thickness of the sample, cm.

D = Diameter of the sample, cm.

The instrument used was INSTRON 1195 model.

The loading parameters are followings:

Cross head speed = 0.5 mm/ min.

Chart speed = 20 mm/ min .

CHAPTER - V

EXPERIMENTAL RESULTS

1. SELECTION OF THE PHOSPHATE BOND FOR SILICON CARBIDE.

Monoaluminium phosphate (MAP) and chromium-aluminium phosphate (CAP) of different compositions were prepared by heating the chemicals for 10 days at 150°C. Alumina from different sources were used for the bond preparation. The compositions of the bonds and their densities are shown in Table V-1. Not unexpectedly, the rate of reaction of H_3PO_4 with Al_2O_3 from ammonium alum was rapid, with Bayer's alumina slow and with pure fused alumina almost negligible.

All these bonds were tried with 3F and C SiC powder in the amount of 12 wt% each. The 5 cm. diameter disc shaped samples were made by using a total load of 5 tonnes (effective pressure = 254.7 Kg/cm^2). After curing, samples were broken in Brazilian test and the tensile strengths were computed. The results are shown in Table V-2. The highest strength was obtained with the bond X_1 , made from H_3PO_4 and fused alumina, in which the reaction was negligible. It was therefore assumed that it was in fact the unreacted H_3PO_4 which acted as the bond.

Table V-1

Preparation of Phosphate Bonds by Heating

 Al_2O_3 , CrO_3 and 90% H_3PO_4 for 10 days at 150°C .

Bond No.	Source of Alumina	Composition (wt%)				Molar ratio $\text{P}_2\text{O}_5:\text{Al}_2\text{O}_3:\text{Cr}_2\text{O}_3$	Bond density gm.cm^{-3}
		Al_2O_3	P_2O_5	Cr_2O_3	H_2O		
X_1	Fused Alumina	11.64	48.58	-	39.78	3:1:0	1.47
X_2	Bayer's Alumina	11.64	48.58	-	39.78	3:1:0	1.50
X_3	Ammonium Alum Alumina	11.64	48.58	-	39.78	3:1:0	1.55
C_1	Bayer's Alumina	10.87	45.41	3.90	39.83	3:1:0.25	1.57
C_2	Ammonium Alum Alumina	10.87	45.41	3.90	39.83	3:1:0.25	1.59
D_1	Bayer's Alumina	10.16	42.45	7.57	39.82	3:1:0.50	1.52
D_2	Ammonium Alum Alumina	10.16	42.45	7.57	39.82	3:1:0.50	1.65
E_1	Bayer's Alumina	9.5	39.9	10.70	39.90	3:1:0.75	1.53
E_2	Ammonium Alum Alumina	9.5	39.9	10.70	39.90	3:1:0.75	1.60

Table V-2

Tensile strength of 3F and C Silicon Carbide
bonded with different phosphate bonds.

SiC : 3F and C, Phosphate bond : 12 wt%

Sample diameter : 5 cm.

Moulding pressure : 5 tons.

Dried : 110°C for 24 hours.

Fired: 600°C for 5 hours.

Bond No.	Thickness (cm)	Fracture load (Kg)	Tensile strength (Kg.cm ⁻²)
X ₁	1.74	595	43.23
X ₂	1.75	414	30.09
X ₃	1.70	445	33.35
C ₁	1.75	345	25.08
C ₂	1.73	354	25.73
D ₁	1.77	289	21.00
D ₂	1.76	330	24.00
E ₁	1.75	336	24.40
E ₂	1.75	420	30.53

The other bonds which gave good results were X_3 (MAP), C_2 (CAP-I) and E_2 (CAP-III) and hence were selected for further trial.

✓ Orthophosphoric acid of 90% concentration (density = 1.72 gms/ cc) and the above mentioned three bonds were tried with 3F and C SiC in the amounts of 12 wt% each. The moulding load was 3 tonnes on 5 cm. dia. samples (effective pressure = 152.83 Kg/cm^2). The samples were cured for 5 hours at temperatures of 400°C , 600°C and 800°C and the strengths were determined. These results are shown in Figure V-1 and the data is in Table A-1 in appendix. At all the temperatures tested, phosphoric acid gave the highest strength, and the strength increased with increasing firing temperature. For CAP-I and CAP-III bonds also, strength increased with increasing curing temperature. But in the case of MAP highest strength was obtained at 600°C . It was therefore concluded that phosphoric acid is the most promising bond for silicon carbide bodies.

2. SELECTION OF THE OPTIMAL COMBINATION OF PHOSPHATE BOND AND BONDING MATRIX (PRELIMINARY SCREENING).

It was felt that, along with a phosphate bond, a fine powder bonding matrix is essential to bind the relatively coarse SiC aggregates and give sufficient strength to the body. To confirm this, SiC aggregates (Batch 1)

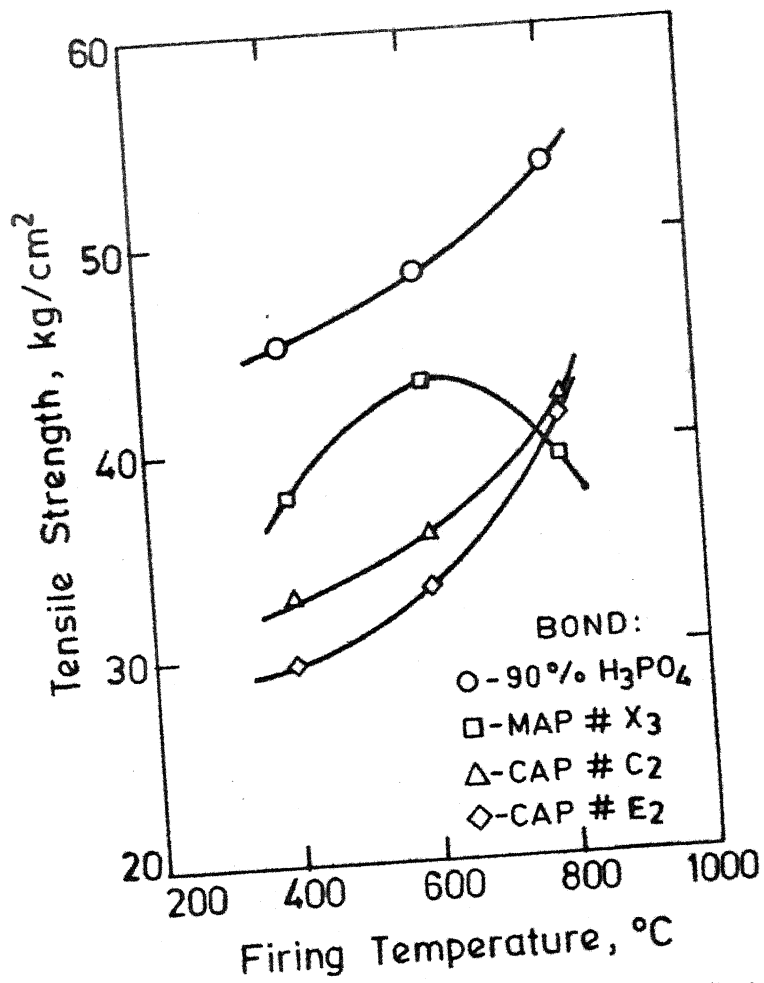


Fig. V-1 Tensile strength of 3F & C SiC bonded with four phosphate bonds.
 (SiC: 3F & C, Bond: 12% wt., Moulding pressure: 3 Tons, Dried: 110°C for 22 hrs., Soak time: 5 hrs, sample dia: 5 cm)

and 3F and C SiC were bonded with phosphoric acid . The samples were pressed under a total load of 20 tons (effective pressure = 1018.8 Kg/ cm^2) and cured at 400°C , 600°C and 800°C temperatures. The tensile strengths are shown in Figure. V-2 and the data in Table A-2 in appendix. The very low strengths of body made from SiC aggregate only clearly demonstrated that a fine grained bonding matrix is necessary.

In many applications e.g. grinding wheels, rubbing stones, abrasion resistance lining etc, it is not necessary that the bonding matrix be also of SiC. A number of cheap and readily available materials such as fly ash, clay, glass etc, known to bind well with phosphate bonds, were next tried. For preliminary screening and in order to save time, a qualitative evaluation procedure was adopted as under.

The fine bonding powders were mixed with different phosphate bonds (see Table V-3 for list) and about 20-30 mm dia. pellets were formed by hand rolling. After curing at three temperatures, the quality of bonding strength attained was ascertained by dropping the pellets on floor from a fixed height and by the scratch test , The results are shown in Table V-3. Promising results were obtained with following powder-bond combinations :

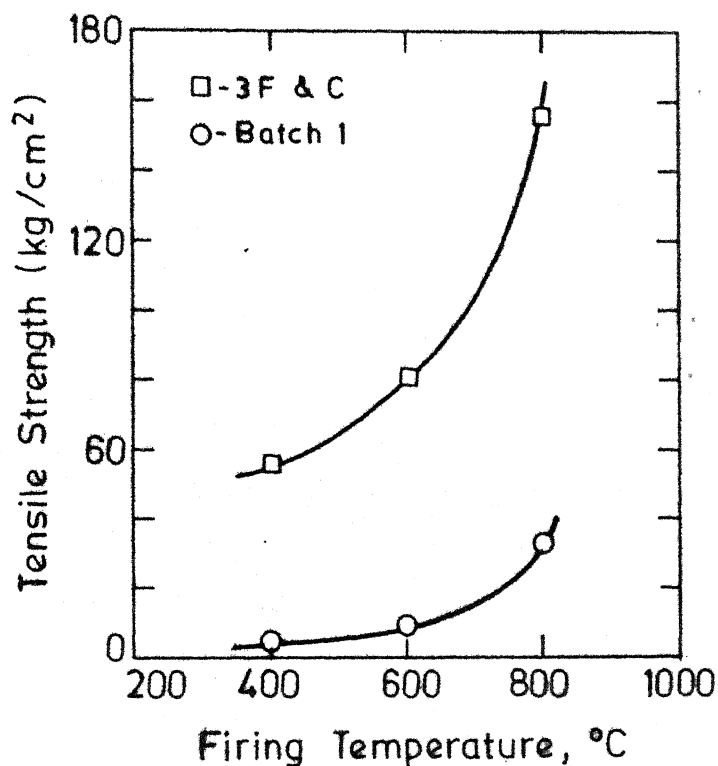


Fig. V-2: Tensile strength of silicon carbide bodies (i) 3F & C and (ii) Batch 1 only bonded with H_3PO_4 .

SiC Batch 1:

Grit: 14/30 - 55%

36/70 - 10%

100 - 10%

200/270 - 10%

270/400 - 15%

Moulding Pressure: 20 Tons

Dried: 120°C for 18 hrs

Soak Time: 5 hrs

Sample dia: 5 cm

Table V-3

Qualitative strength evaluation of different **fine** bonding matrices and phosphate bond combinations.

Firing temp. °C.	wt% bonds						
	H ₃ PO ₄					Na(PO ₃) ₆	(NH ₄) ₂ HPO ₄
	4.5	6.75	9	20	77.5	20	20
Fly ash matrix							
400	Low	Low	Low	Low	Low	Low	Low
500	Low	Low	Low	Low	Low	Low	Low
600	Low	Low	Low	Low	Low	Low	Low
Window glass matrix							
400	Low	Low	Low	Low	Low	Low	Very low
500	Low	Low	Low	Low	Low	Fair	Very low
600	Low	Low	Low	Low	Low	Good	Very low
Calcined clay matrix							
400	Fair	Good	Good	High	-	Soft	Good
500	Fair	Good	Good	High	-	Soft	Good
600	Good	Good	Good	High	-	Fair	Good
Thermit slag matrix							
400	Very low	Low	Low	Good	-	Soft	Soft
500	Very low	Low	Low	Good	-	Soft	Soft
500	Very low	Low	Low	Good	-	Fair	Soft

calcined clay- H_3PO_4 ; calcined clay- $(\text{NH}_4)_2\text{HPO}_4$; thermit slag- H_3PO_4 and window glass- $(\text{NaPO}_3)_6$. It was then decided to try out these combinations to see how well these bind SiC aggregates.

Silicon carbide samples (Batch No. 2,3 and 4) were made with the above combinations under a total load of 2 tonnes (effective pressure = 101.9 Kg/cm^2) and cured at 600°C for 5 hours. A qualitative evaluation, as before, indicated that calcined clay- H_3PO_4 combination with 26% H_3PO_4 gave the best results, as shown in Table V-4.

In order to obtain more definite conclusions, we next decided to bind different matrix material powders with H_3PO_4 and MAP (prepared from ammonium alum alumina) and test their strengths quantitatively. Samples of 2.5 cm. dia. were made under a total load of 3 tonnes (effective pressure = 611 Kg/cm^2) and cured at different temperatures and tested for the tensile strengths. The results are shown in Figures V-3 and V-4 and data in Table A-3 in appendix. Good strength values were obtained with Pyrex glass-MAP, Pyrex glass- H_3PO_4 , calcined talc-MAP, calcined talc- H_3PO_4 , thermit slag-MAP and thermit slag- H_3PO_4 combinations. However the amount of liquid bond required in case of pyrex glass was very high (47%). Thus the most promising bonding matrices seemed to be thermit slag, calcined talc (and calcined clay and fine SiC from earlier experiments) with H_3PO_4 or MAP bond.

Table V-4

Qualitative strength of silicon carbide bodies bonded with different matrix-bond combinations.

Composition:

SiC batch - 100 weight units

Matrix powder- 22 weight units

SiC Batch 2:	SiC Batch 3:	SiC Batch 4:
Grit:	Grit:	Grit:
36/70-26%	14/30-40%	7/12-45%
100 - 74%	36/70-44%	14/30-40%
	100 -16%	100 -15%

Sample diameter : 5 cm .

Moulding pressure : 2 tons.

Dried : 110°C for 24 hours.

Fired : 600°C for 5 hours.

Liquid bond wt% of bonding matrix)	Bonding matrix	Relative strength		
		SiC	Batch	
		2	3	4
P_2O_5 (13%)	Calcined clay	Fair	Fair	Fair
P_2O_5 (26%)	Calcined clay	Good	Good	Good
$NH_4)_2HPO_4$ (45%)	Calcined clay	Fair	Fair	Fair
P_2O_5 (40%)	Thermit slag	Fair	Fair	Fair
$NaPO_3)_6$ (45%)	Window glass	Low	Low	Low

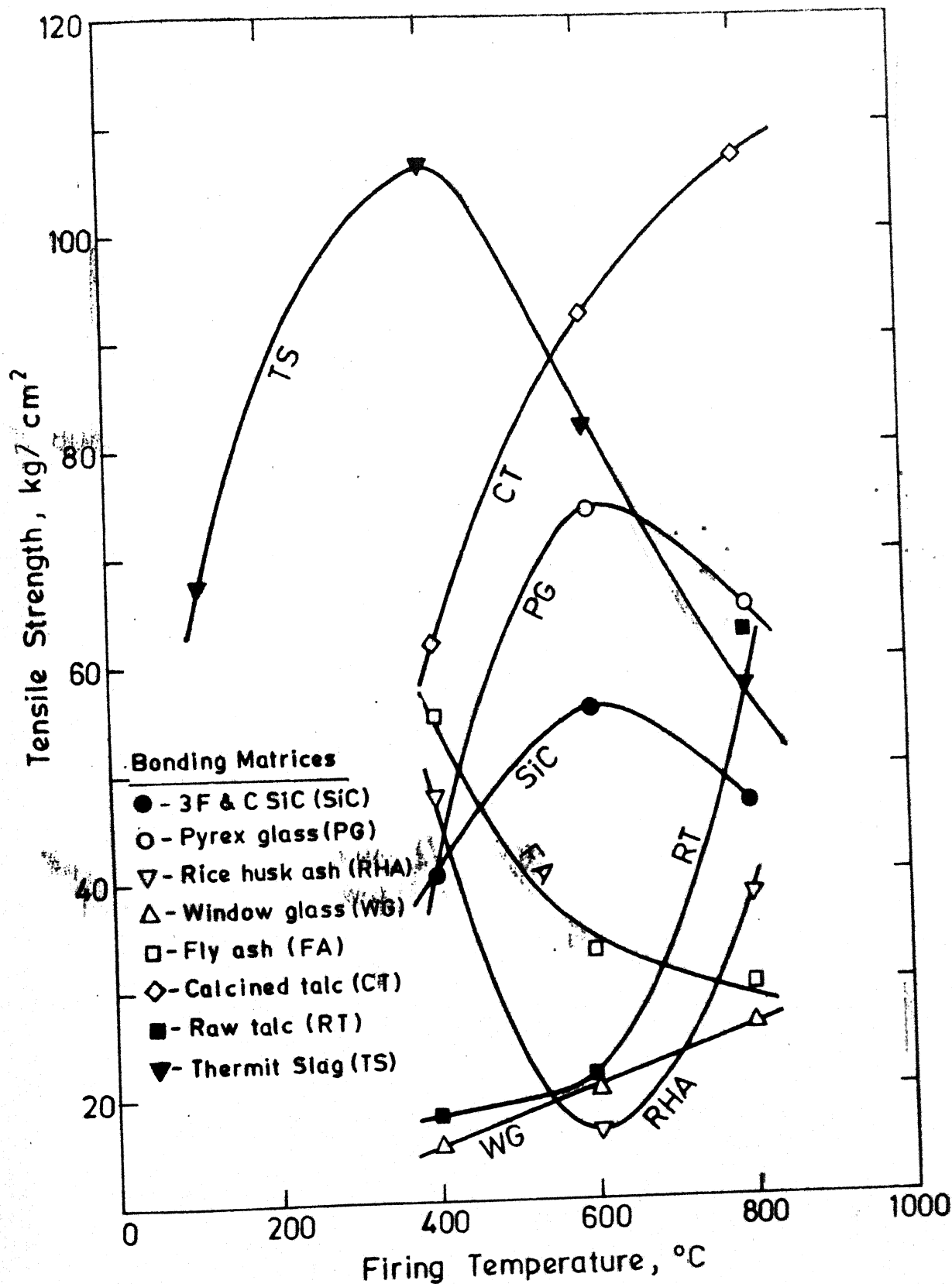


Fig. V-3: Tensile strengths of different fine bonding matrices with monoaluminium phosphate.
 (Moulding Pressure: 3 Tons, Dried: 110°C for 24 hrs, Soak time: 5 hrs.
 Sample dia: 2.5 cm)

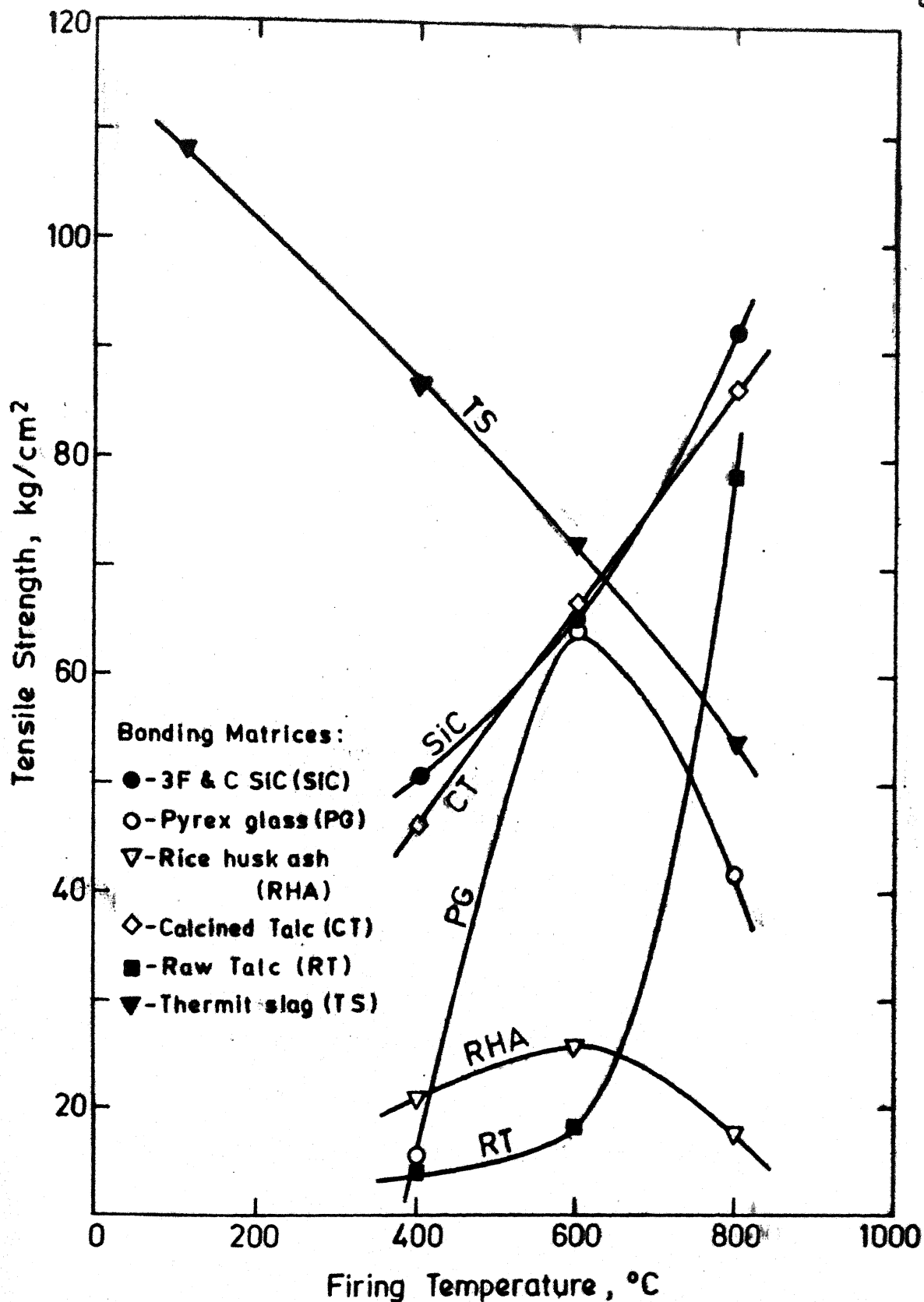


Fig. V-4: Tensile strengths of different fine bonding matrices with H_2
 (Moulding pressure : 3 Tons, Dried: 110°C for 24 hrs, Soak time : 5 hrs,
 Sample dia: 2.5 cm)

3. SELECTION OF OPTIMAL BONDING MATRIX FOR SILICON CARBIDE AGGREGATES.

Above results lead to the intriguing possibility of a mixed matrix bond comprising of fine SiC plus one of the other three candidates. Accordingly, SiC (Batch 2) was bonded with 3F and C SiC and calcined clay mixed matrix in different proportions and H_3PO_4 . 5 cm dia. discs were made under a load of 3 tonnes (effective pressure = 152.8 Kg/cm^2). After curing at three temperatures, the bulk density and tensile strength values were determined. The strengths are given in Figure V-5 and data in Table A-4 in appendix. Since best results were obtained with 100% 3F and C matrix or 75% 3F and C + 25% calcined clay matrix at 800°C , these matrices were chosen for binding other silicon carbide batches also and tested after curing at 800°C since general maximum strength was attained at 800°C . The tensile strength results are given in Table V-5.

Mixed matrices of 3F and C SiC- calcined talc and 3F and C SiC- thermit slag in different proportions and bonded with H_3PO_4 and MAP were also tested with SiC batch-2 body. The amount of powder matrix used was 33 weight units with 100 weight units of SiC aggregate and

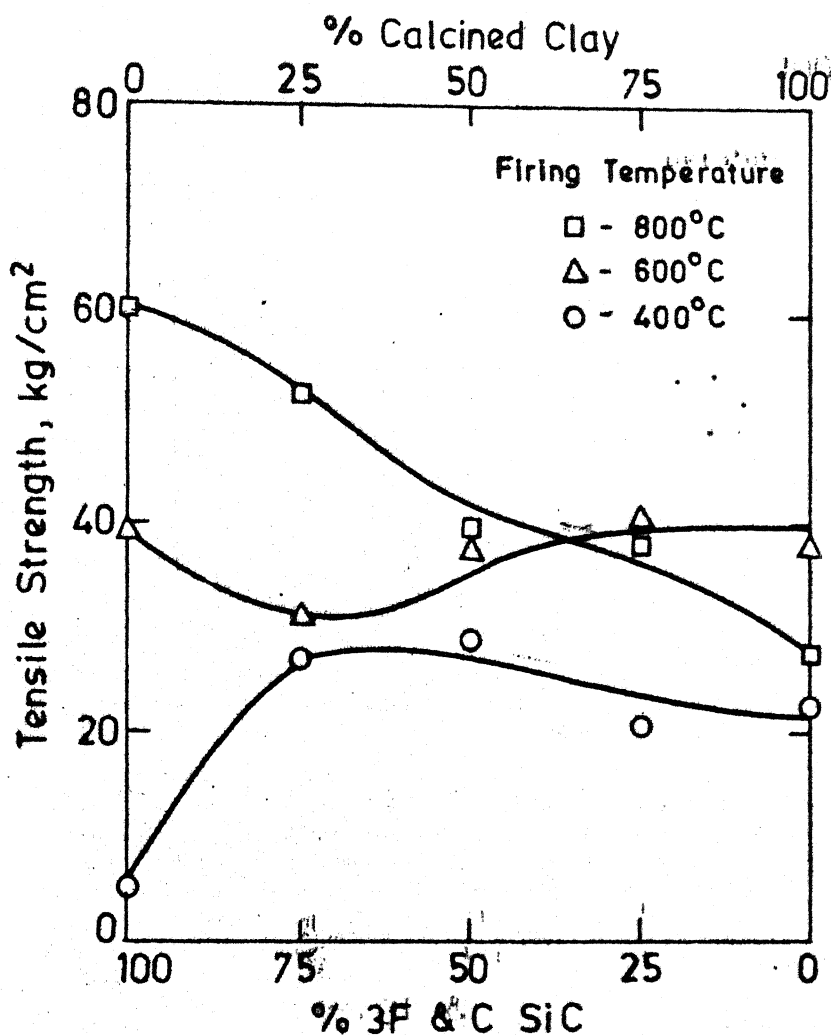


Fig. V-5: Tensile strengths of SiC Batch 2 body bonded with 3F & C SiC-calcined clay matrix of different proportions and H_3PO_4 .

Composition :

SiC Batch 2 - 100 weight units

Calcined clay - 33 weight units

H_3PO_4 (wt. % of clay) - 40

Moulding pressure : 3 Tons, Dried: $110^\circ C$ for 24 hrs

Soak time: 5 hrs, Sample dia: 5 cm

Table V-5

Tensile strengths of three silicon carbide bodies bonded with 100% 3F and C SiC and 75% 3F and C SiC + 25% calcined clay matrix.

Composition:

SiC Batch - 100 weight units
 Matrix powder-33 weight units
 Phosphate bond (wt% of matrix powder)
 $\text{-H}_3\text{PO}_4$ (40%)

Sample diameter : 5cm.
 Moulding pressure : 3 tons,
 Dried : 110°C for 24 hours,
 Fired : 800°C for 5 hours.

Powder matrix		Base Composition	Bulk density (gms/cc)	Tensile Strength (kg/cm ²)
3F and C SiC (%)	Calcined clay (%)	Batch No.		
100	0	2	2.05	62.94
			2.00	58.00
75	25	2	2.11	59.98
			2.09	55.22
100	0	3	2.43	69.70
			2.41	72.43
75	25	3	2.37	57.44
			2.25	57.12
100	0	4	2.38	55.20
			2.41	57.14
75	25	4	2.31	54.32
			2.23	53.17

the phosphate bond added was 40% on the basis of powder matrix. The samples of 2.5 cm dia. were made under a total load 1 tonne (effective pressure = 203.6 Kg/cm^2) and cured at 400°C , 600°C and 800°C . The resulting tensile strengths are shown in Figures V-6 and V-7 and the data in Tables A-5 and A-6 in appendix. It was concluded that (i) H_3PO_4 is superior than MAP, (ii) Strengths are highest at 800°C , (iii) the best mixed matrix contains 75% SiC and 25% calcined talc or thermit slag and (iv) tensile strength approaching 100 Kg/cm^2 can be attained. These two mixed matrices were tested with all the three SiC batches and at higher moulding pressure.

The amount of powder matrix used was 40 weight units for 100 weight units of SiC aggregates and the phosphate bond added was 40% of the matrix powder. The moulding load on 2.5 cm dia. samples was 4 tonnes (effective pressure = 815 Kg/cm^2) . The tensile strengths are shown in Figure V-8 and data is in Table A-7 in appendix.

SiC Batch-3 samples gave best results; the tensile strength exceeded 150 Kg/cm^2 at 800°C with both bonding matrices. Hence SiC Batch 3 body was selected to determine the effect of the amount of bonding matrix and moulding pressure on strength.

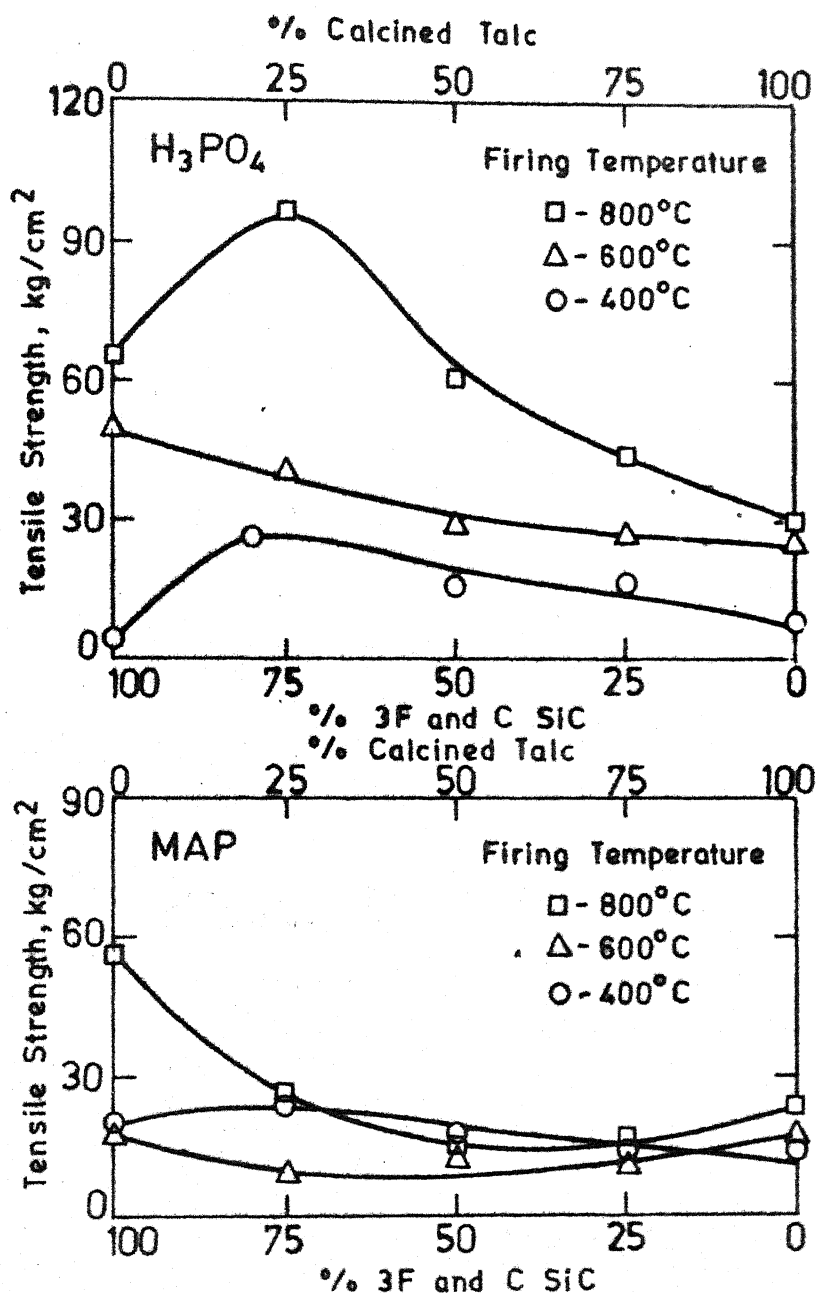


Fig. V-6: Tensile strengths of SiC batch 3 body bonded with 3F & C SiC-calcined talc matrix of different proportions and H₃PO₄ and monoaluminium phosphate

Composition:

SiC Batch 3 - 100 weight units

Calcined talc - 33 weight units

H₃PO₄ (wt. % talc) - 40

Moulding pressure: 1 Ton, Dried: 110°C for 24 hours

Soak time: 5 hours, Sample dia: 2.5 cm.

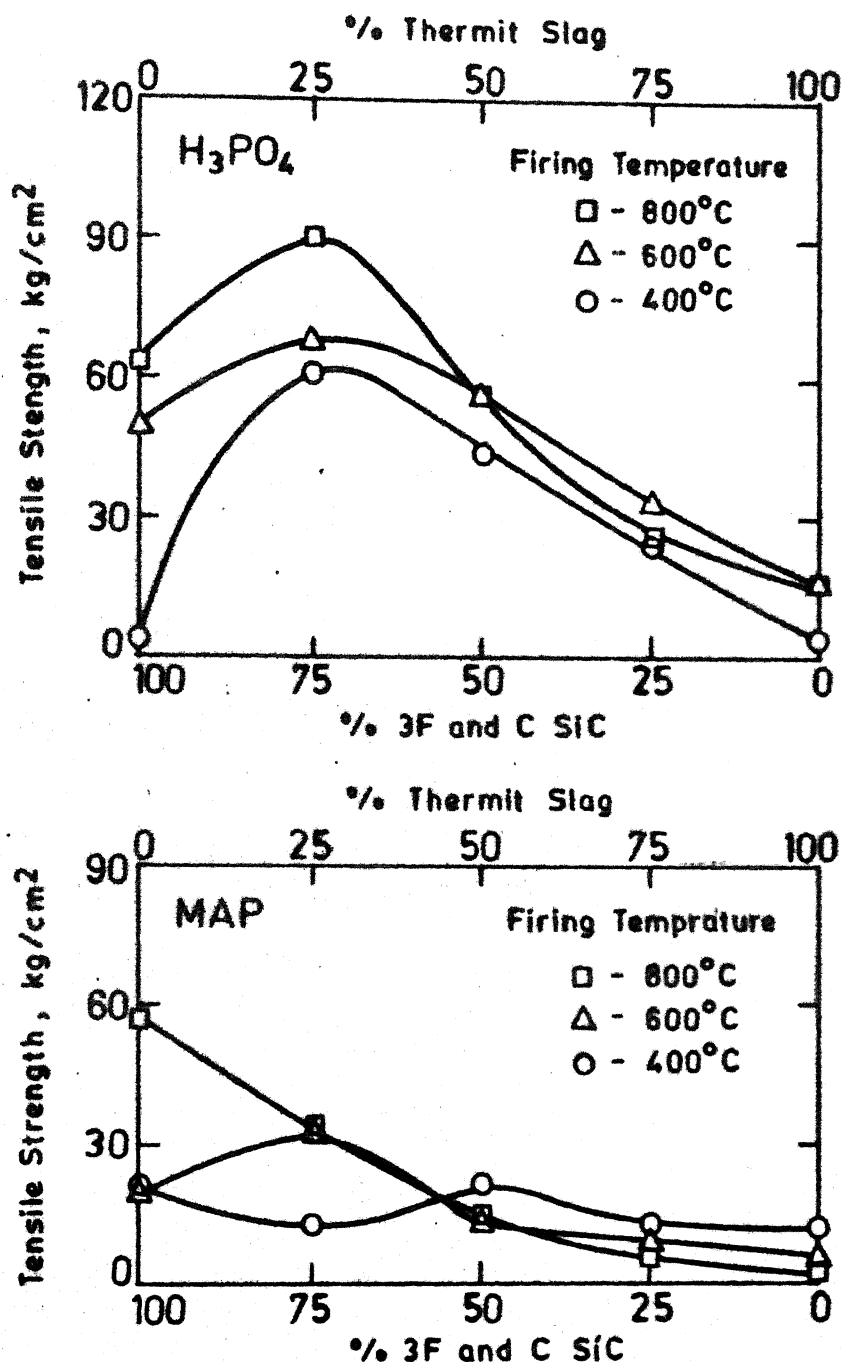


Fig. V-7: Tensile strengths of SiC batch 3 body bonded with 3F & C SiC -thermit slag matrix of different proportions and H₃PO₄ and monoaluminium phosphate.

Composition:

SiC Batch 3 - 100 weight units

Thermit slag - 33 weight units

H₃PO₄ (wt. % slag) - 40

Moulding pressure: 1 ton, Dried: 110°C for 24 hrs

Soak Time: 5 hours, Sample dia: 2.5 cm

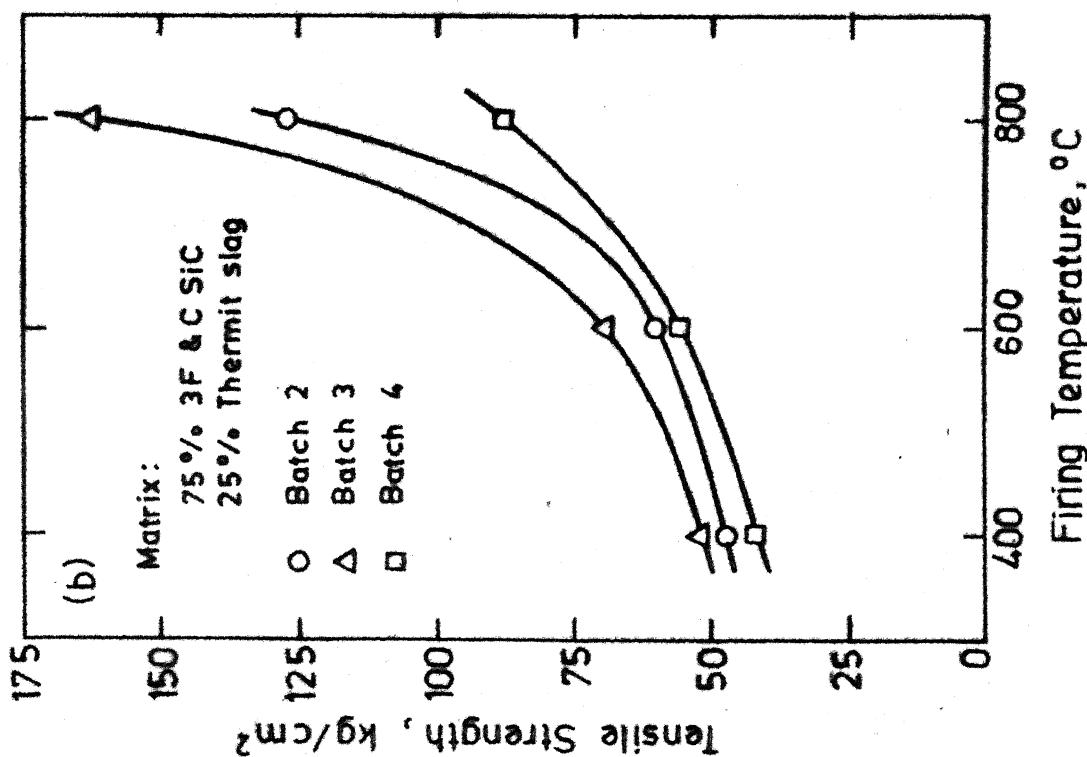
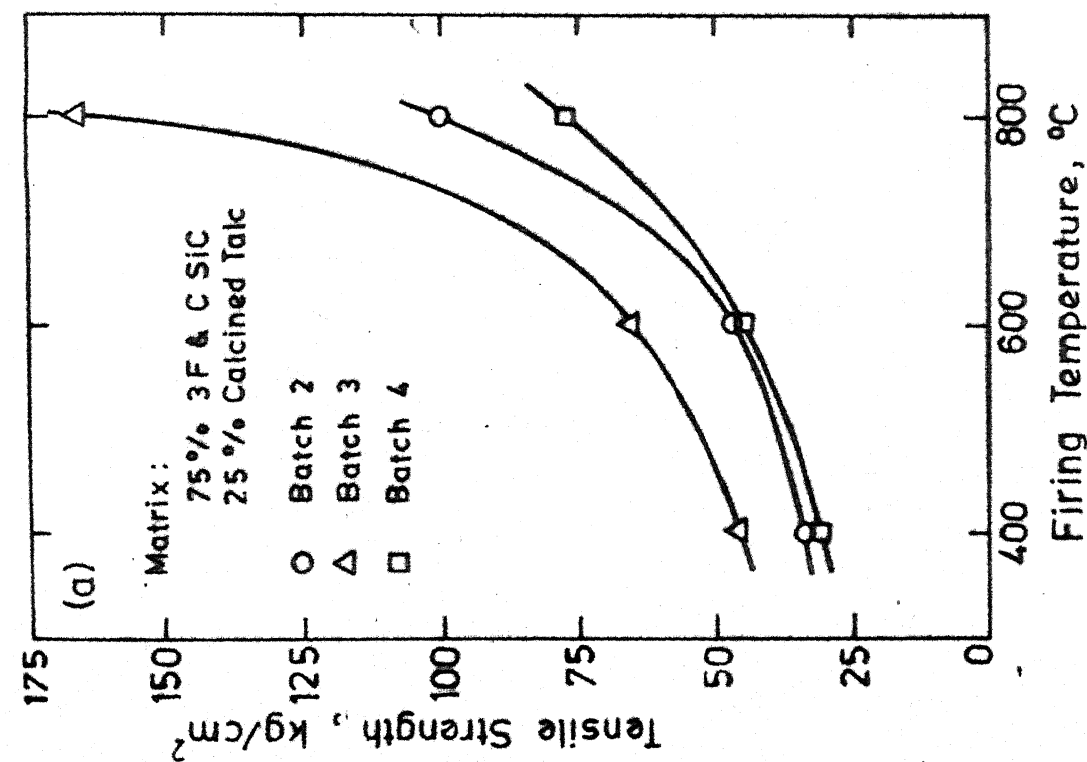


Fig. V-8: Tensile strengths of silicon carbide bodies bonded with (a) 75% 3F & C SiC-25% calcined talc and (b) 75% 3F & C SiC-25% thermit slag matrices with H_3PO_4 .

Composition: SiC batch - 100 weight units. Matrix powder - 40 weight units.

H_3PO_4 (wt % matrix powder) = 48%

Moulding pressure: 4 Tons, Dried: 110°C for 30 hrs, Soak time: 5 hrs. Sample dia: 25 mm

4. EFFECT OF AMOUNT OF BONDING MATRIX , MOULDING PRESSURE AND CURING TEMPERATURE ON STRENGTH OF PHOSPHATE BONDED SILICON CARBIDE.

Silicon carbide Batch 3 samples of 2.5 cm.dia. were bonded with 75% 3F and C SiC +25% calcined talc matrix and 75% 3F and C SiC +25% thermit slag matrix and H_3PO_4 . In 100 weight units of SiC Batch 3, the weight units of powder matrix were 26, 33 and 40. The amount of H_3PO_4 on wt% of powder matrix were 50% when the total moulding load is 1 tonne (effective pressure = 203.6 Kg/cm^2) and 48% when the load is 4 tonnes (effective pressure = 815 Kg/cm^2). The samples were fired for 5 hours at 600°C , 800°C and also 1000°C . The tensile strengths are shown in Figures V-9 and V-10, and the data is in Tables A-8 and A-9 in appendix.

Understandably , the strength was always higher with larger amount of the bonding matrix. The optimal curing temperature was 800°C , in fact strength drops rather rapidly at 600°C and 1000°C . Interestingly the moulding pressure did not seem to have a marked effect. The best results were obtained with samples pressed at 4 tonnes. In fact at higher pressure of 10 tonnes (Tables A-8 and A-9 in appendix) strength was lower which could be due to the lower liquid bond content of these samples. Since at higher pressures, liquid content had to be reduced to prevent bleeding off

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Table A-1

Variation of tensile strength with firing temperature for 3F and C, silicon carbide bonded with different phosphate bonds.

Sic: 3F and C, Phosphate bond : 12 wt%.

Sample diameter : 5 cm.

Moulding pressure : 3 tons

Dried : 110°C for 22 hours.

Soak time: 5 hours.

Bond	Tensile strength (Kg.cm ⁻²), when fired at		
	400°C	600°C	800°C
H ₃ PO ₄ (90%) density = 1.72 gm/cm ³	45.1	48.3	53.4
X ₃	37.8	43.0	39.2
C ₂	32.7	35.6	42.1
E ₂	29.8	33.4	41.4

Table A-2

Tensile strengths of silicon carbide bodies bonded
with H_3PO_4 (90%) at three temperatures.

SiC Batch 1 :

Grit: 14/30 - 55%
36/70 - 10%
100 - 10%
200/270- 10%
270/400- 15%
(3F and C)

Sample diameter : 5 cm.

Moulding pressure: 20 tons.

Dried : 120°C for 18 hours.

Soak time : 5 hours.

Bond (wt%)	SiC body	Tensile strength (Kg.cm^{-2}) , when fired at		
		400°C	600°C	800°C
12	3F and C	55.24	80.34	156.30
7.5	Batch.1	4.30	9.45	33.43

Variation of tensile strengths of different phosphate bonded powder matrices with temperature.

Moulding pressure : 3 tons . Sample dia: 2.5 cm.

Dried : 110°C for 24 hours,

Soak time : 5 hours .

Powder matrix	Liquid bond (wt%)		Tensile strength (Kg/cm ⁻²), when fired at			
	Mono Alu- minium Phosphate	H ₃ PO ₄	110°C	400°C	600°C	800°C
3F and C SiC	15	-	-	41.50 39.23	55.73 55.16	46.50 45.93
3F and C SiC	-	15	-	50.47 49.86	64.91 65.01	92.65 92.42
Pyrex Glass	47	-	-	41.63 39.32	72.67 76.19	67.34 63.57
Pyrex Glass	-	47	-	15.24	64.16	41.34
Window Glass	60	-	-	14.50 16.06	19.40 21.20	27.30 25.40
Fly Ash	14	-	-	50.50 60.40	32.53 33.50	30.18 29.35
Rice Husk Ash	40	-	-	58.15 37.18	14.84 17.75	40.00 36.21
Rice Husk Ash	-	40	-	20.35	24.68 26.85	17.34 18.02
Calcined Clay	38	-	-	Cracks	Cracks	Cracks
Calcined Talc	25	-	-	67.23 56.00	92.22	95.00 106.40
Calcined Talc	-	25	-	45.79 50.39	57.00 76.32	94.70 78.00
Raw Talc	20	-	-	17.50 18.90	21.50 21.42	51.39 74.59
Raw Talc	-	20	-	14.13	18.09	78.32
Thermit Slag	22	-	67.29	97.80 114.50	80.60 83.06	54.00 60.60
Thermit Slag	-	22	108.00	87.46 85.55	75.11 69.26	56.37 48.73

Table A-4

Tensile strengths of silicon carbide bodies bonded with 3F and C SiC and calcined clay matrix of different composition with H_3PO_4 .

Composition :

SiC Batch 2 - 100 weight units.

Matrix powder - 33 weight units.

Phosphate bond (wt% of matrix powder)

Sample diameter : 5 cm. - H_3PO_4 (40%).

Moulding pressure : 3 tons.

Dried : 110°C for 24 hours.

Soak time : 5 hours.

wder matrix mposition		Bulk density(gm.cm ⁻³) when fired at			Tensile strength(Kg.cm ⁻²) when fired at		
and C SiC (%)	Calci- ned Clay (%)	400°C	600 °C	800°C	400°C	600°C	800°C
00	0	2.02 2.12	2.02 2.01	2.05 2.00	5.09 5.80	40.37 38.84	62.94 58.00
75	25	2.06 2.13	2.12 2.12	2.11 2.09	24.75 30.00	31.11 31.01	59.98 55.22
50	50	2.10 2.09	2.10 2.11	2.13 2.07	32.92 25.44	37.39 36.38	42.60 36.99
25	75	2.08 2.16	2.21 2.12	2.06 2.09	21.01 21.08	42.32 39.16	37.92 38.07
0	100	2.09 2.12	2.19 2.19	2.11 2.10	23.13 21.60	37.91 38.44	30.12 25.39

Table A-5

Tensile strengths of silicon carbide bodies bonded with 3F and C SiC and calcined talc matrix of different composition and H_3PO_4 and monoaluminium phosphate (MAP).

Composition : SiC Batch 2- 100 weight units.
 Matrix powder-33 weight units.
 Phosphate bond (wt% of matrix powder) $-H_3PO_4$ (40%).
 Sample diameter : 2.5cm.
 Moulding pressure : 1 ton
 Dried : 110°C for 24 hours.
 Soak time : 5 hours.

Powder Matrix		Phosphate Bond	Tensile strength ($Kg.cm^{-2}$), when fired at		
3F and C SiC (%)	Calcined Talc (%)		400°C	600°C	800°C
00	0	H_3PO_4	4.85	50.09	64.85
			4.02	50.13	64.51
75	25	H_3PO_4	29.76	43.94	98.32
			22.39	37.69	95.54
50	50	H_3PO_4	16.48	28.82	58.42
			14.68	29.07	62.47
25	75	H_3PO_4	16.96	25.44	45.43
			16.07	28.51	43.59
0	100	H_3PO_4	9.25	23.85	42.40
			5.80	24.42	47.31
00	0	MAP	21.37	20.59	59.17
			22.39	19.08	56.95
75	25	MAP	22.63	9.20	25.40
			27.14	9.71	28.62
50	50	MAP	18.93	10.58	17.90
			16.71	12.72	15.23
25	75	MAP	13.23	11.62	14.42
			14.25	10.67	19.48
0	100	MAP	13.70	18.28	25.82
			14.84	16.30	21.36

Table A-6

Tensile strength of silicon carbide bodies bonded with 3F and C SiC and thermit slag matrix of different composition and H_3PO_4 and monoaluminium phosphate (MAP).

Composition :

SiC Batch 2- 100 weight units,
Matrix powder -33 weight units,
Phosphate bond (wt% of matrix powder)

Sample diameter : 2.5 cm. - H_3PO_4 (40%),
Moulding pressure : 1 ton.
Dried : 110°C for 24 hours,
Soak time : 5 hours.

Powder Matrix		Phosphate Bond	Tensile strength (Kg. cm ⁻²), when fired at		
3F and C SiC (%)	Thermit Slag (%)		400°C	600°C	800°C
100	0	H_3PO_4	4.85 4.02	50.09 50.13	64.85 64.51
75	25	H_3PO_4	60.23 62.25	67.00 70.23	90.20 90.55
50	50	H_3PO_4	39.04 49.36	50.40 63.15	57.95 57.44
25	75	H_3PO_4	20.65 27.11	36.14 30.53	24.93 28.59
0	100	H_3PO_4	4.68 4.98	17.34 16.96	19.27 16.46
100	0	MAP	21.37 22.39	20.59 19.08	59.17 56.95
75	25	MAP	12.13 13.69	31.52 32.56	30.97 37.64
50	50	MAP	22.49 20.90	13.72 12.21	12.90 16.54
25	75	MAP	13.05 11.56	8.55 9.27	10.60 12.16
0	100	MAP	11.06 12.92	5.63 5.87	4.82 4.35

Table A-7

Tensile strengths of 3 silicon carbide bodies bonded with 75% 3F and C SiC + 25% calcined talc matrix and 75% 3F and C SiC + 25% thermit slag matrix with H_3PO_4 .

Composition :
SiC Batch - 100 weight units ;
Matrix powder-40 weight units.

Sample diameter : 2.5 cm.
Moulding pressure : 4 tons.
Dried : 110°C for 30 hours.
Soak time : 5 hours.

Batch No.	Matrix Powder			H_3PO_4 (wt.% of matrix powder)	Tensile strength (Kg.cm ⁻²), when fired at		
	3F and C SiC (%)	Calcined Talc (%)	Thermit Slag (%)		400°C	600°C	800°C
2	75	25	-	48	36.34 32.22	48.64 43.61	106.18
3	75	25	-	48	40.06 49.36	65.13 66.03	165.10 169.11
4	75	25	-	48	29.52 36.31	50.09 42.13	79.43 72.65
2	75	-	25	48	52.11 44.24	57.24 64.76	128.25 126.05
3	75	-	25	48	50.40 54.51	72.24 65.35	169.60 155.50
4	75	-	25	48	38.31 41.52	53.90 57.72	83.64 92.19

Table A-8

Variation of tensile strengths of silicon carbide bodies with amount of powder matrix, firing temperature and moulding pressure:

Composition :

SiC Batch 3 - 100 weight units.
Powder matrix- 75% 3F and C SiC and 25%
Calcined talc.
Phosphate bond $\text{-H}_3\text{PO}_4$

Sample diameter : 2.5 cm.
Dried : 110°C for 30 hours.
Soak time : 5 hours.

Moulding Pressure (Tons)	Powder Matrix (wt.units)	H_3PO_4 (wt% of powder matrix)	Tensile strength (Kg.cm^{-2}), when fired at		
			600°C	800°C	1000°C
1	26	50	16.23	74.19	34.62
			14.55	68.61	33.73
1	33	50	47.33	93.29	40.32
			41.67	97.18	39.27
1	40	50	48.51	144.94	56.77
			49.29	139.12	51.39
4	26	48	30.16	104.61	53.35
			23.54	101.19	47.64
4	33	48	48.29	131.59	49.46
			48.55	126.38	47.75
4	40	48	67.92	172.37	57.97
			74.59	161.68	53.93
10	40	32	68.81	93.45	48.19
			68.03	99.81	43.67

Table A-9

Variation of tensile strengths of silicon carbide bodies with amount of powder matrix, firing temperature and moulding pressure.

Composition : SiC Batch 3- 100 weight units.
Powder matrix- 75% 3F and C SiC and 25% thermit slag .
Phosphate bond - H_3PO_4 .

Sample diameter : 2.5 cm.
Dried : 110°C for 30 hours.
Soak time : 5 hours.

Moulding Pressure (Tons)	Powder Matrix (wt.units)	H_3PO_4 (wt% of powder matrix)	Tensile strength ($Kg.cm^{-2}$), when fired at		
			600°C	800°C	1000°C
1	26	50	52.93	72.31	46.35
			53.68	72.08	48.86
1	33	50	65.49	94.54	42.27
			63.95	97.85	43.71
1	40	50	70.05	112.56	44.91
			74.19	115.00	41.58
4	26	48	60.44	80.55	65.82
			55.39	86.18	61.58
4	33	48	62.64	114.62	48.26
			68.51	105.49	42.95
4	40	48	69.07	153.29	54.15
			74.49	162.84	52.67
10	40	32	65.12	44.28	30.03
			63.74	41.36	34.46

Table A-10

Variation of tensile strengths of oven dried silicon carbide samples with the amount of powder matrix.

Composition :

SiC Batch 3 - 100 weight units.

Powder matrix- thermit slag .

Phosphate bond- H_3PO_4 .

Sample diameter : 2.5 cm.

Moulding pressure : 1 ton.

Curing : 1100°C for 30 hours.

Thermit Slag (wt.units)	H_3PO_4 (wt% of powder matrix)	Tensile strength (Kg.cm ⁻²)
33	50	14.34 14.09
40	50	15.65 16.34
50	50	17.23 17.10

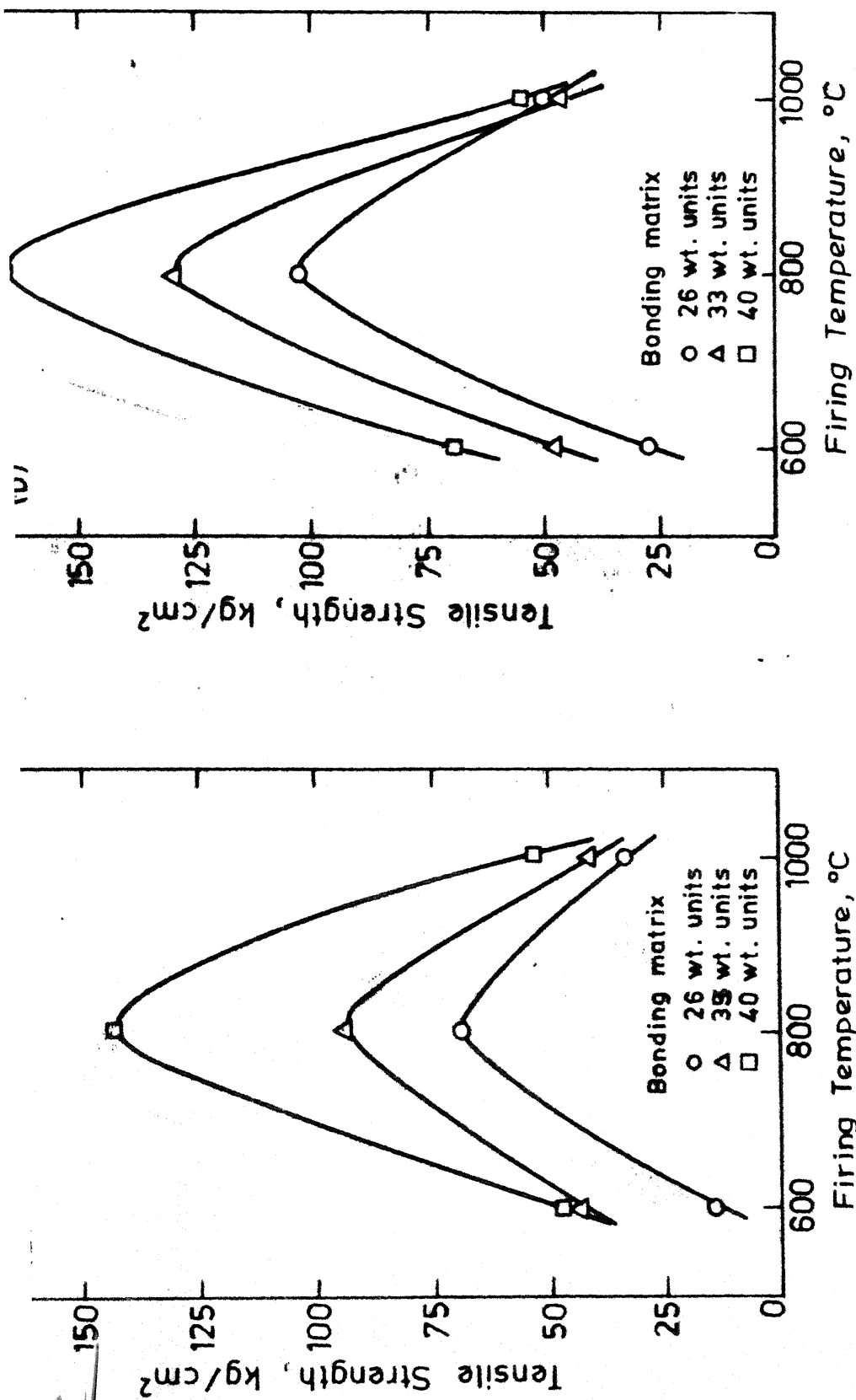


Fig. V-9: Tensile strengths of silicon carbide body as a function of the amount of bonding matrix and firing temperature with (a) 1 Ton moulding pressure (b) 4 Tons moulding pressure.

Composition: SiC batch 3 = 100 wt. units, Bonding matrix: 75% 3F & C SiC + 25% calcined talc
 Dried: 110°C for 30 hrs, soak time: 5 hrs. H_3PO_4 (wt.% bonding matrix):(a) 50% (b) 40%. Sample dia: 2.5 cm.

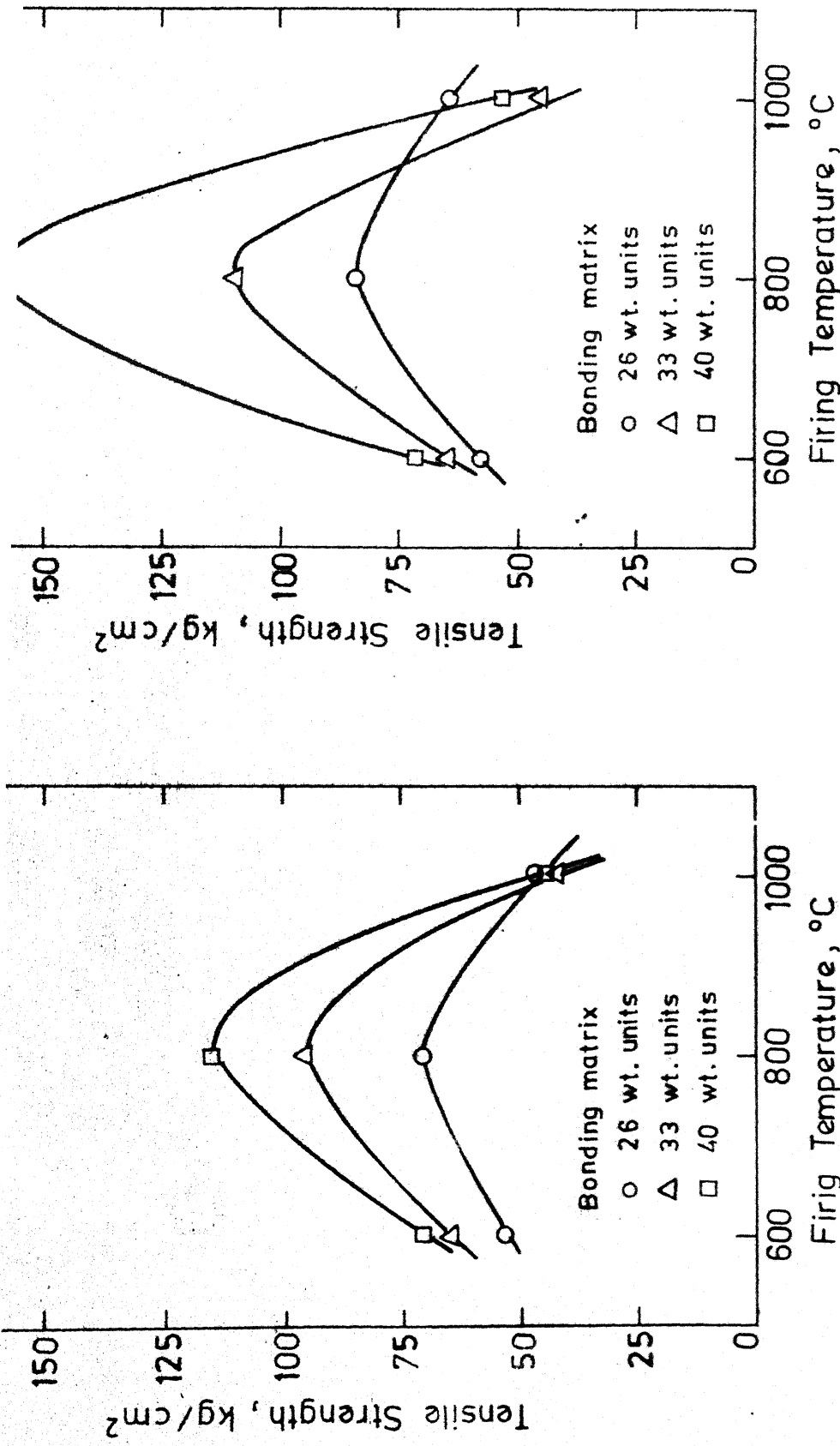


Fig. V-10: Tensile strengths of silicon carbide body as a function of the amount of bonding matrix and firing temperature with (a) 1Ton moulding pressure and (b) 4 Tons moulding pressure.

Compositor : SiC batch 3 = 100 wt. units, Bonding matrix = 75% 3F & C SiC + 25% thermit slag

Dried : 110°C for 30hrs, soak time: 5hrs. H_3PO_4 (wt. % bonding matrix): (a) 50%

(b) 48% Sample dia.: 2.5 cm

and laminations.

It will be seen in Figures V-3, V-4 and Table A-3 that thermit slag samples showed good strength values even after curing at 110°C only and the strength fell with increasing curing temperatures. Trials were therefore done to examine the strength of SiC Batch-3 samples bonded with fine thermit slag and H_3PO_4 after oven drying at 110°C only. The results, shown in Table A-10, were not promising.

Another trial was done with thermit slag base composition (grit 14/30-40%, grit 36/70-44%, grit 100-16%) using fine thermit slag (33 weight units) as the powder matrix and H_3PO_4 (60% on the basis of powder matrix) as the phosphate bond. The samples (2.5 cm.dia.) were made under 1 tonne moulding load and cured in atmosphere and also in an oven at 110°C . The tensile strength values were 59.44 Kg/cm^2 for atmospheric curing and only 32.92 Kg/cm^2 for oven curing . Thus it was not found feasible to make a strong abrasion resistance ceramic out of thermit slag by curing at about 100°C .

CHAPTER -VI

DISCUSSIONS

The mechanism of $\text{SiC-H}_3\text{PO}_4$ reaction is almost totally unknown. An extra complication is the presence of impurities, mainly silica and iron oxides, which tend to concentrate ~~more~~ proportionately more in the fine sizes. To what extent these impurities react with H_3PO_4 and contribute to bonding is also not known. The elucidation of the reaction mechanism was however beyond the scope of this work.

A principal result of this work is that many minerals such as clay and talc which dehydroxylate on heating can be used effectively as bonding matrix with H_3PO_4 in particular and phosphate bonds in general. For best results it would seem that these materials be calcined under controlled temperature conditions. It is well known that the breakdown of the original crystal structure during dehydroxylation results initially in highly distorted crystalline phases or even amorphous phases and these phases exhibit very high degree of reactivity. Also, removal of water in the precalcination stage reduces shrinkage of the final body as well as its porosity.

Combination of fine SiC and precalcined clay or talc have additional advantages.

(i) Workability of the mix is improved because SiC is a highly abrasive and harse material whereas the other two are platy and soft.

(ii) The wear of die is less which is an important consideration in pressing of SiC bodies under high load.

(iii) As pointed out earlier, due to bleeding of liquid bond it was not possible to apply very high moulding pressure. On the other hand, reduction of the liquid content for high pressure moulding resulted in insufficient amount of phosphate bond for reaction. It could turn out that the tendency to bleed would be significantly reduced in presence of talc or clay and therefore for high moulding pressure larger % of these materials should be incorporated in the mixed matrix bond. This point deserves to be investigated further.

Between talc and thermit slag the former is to be preferred for following reasons:

(i) Thermit slag is a very hard material and difficult to grind fine.

(ii) Thermit slag reacts with H_3PO_4 and produces a great deal of heat with a very fast reaction.

(iii) Because of its abrasiveness it contributes nothing to the prolongation of die life.

In these experiments the maximum strength attained was of the order of 160 Kg/cm^2 tensile strength. It is well known that for brittle materials or brittle bonding matrices compressive strength to tensile strength ratio lies between 7-12. Therefore it can be said with the reasonable degree of confidence that the SiC bodies of compressive strength of approximately 1500 Kg/cm^2 can be prepared by curing at 800°C only. For many structural, abrasion resistance liner, abrasive wheels and blocks etc. this magnitude of strength is sufficient. For refractory applications, specially heat exchangers it may turn out that the presence of talc or clay is undesirable in which case it would be necessary to use the single bonding matrix of fine SiC only.

It should be noted that Batch no 2,3 and 4 are not specifically designed for densest possible packing of particles. As a matter of fact, these are standard rubbing stone composition in which packing is not a critical parameter. Therefore it is reasonable to expect that by using dense packing SiC aggregate composition, the compressive strength can be boosted further.

CHAPTER - VII

CONCLUSIONS

On the basis of the experimental work carried out and results obtained therefrom, the following conclusions can be drawn:

(i) Highly strong and abrasion resistance phosphate bonded silicon carbide refractories can be made by firing them at a lower temperature, 800°C .

(ii) A powder bonding matrix and a liquid phosphate bond are used to get good strength.

(iii) 75% 3F and C SiC- 25% calcined talc and 75% 3F and C SiC- 25% thermit slag matrices are best as the powder bonding matrix.

(iv) Phosphoric acid is the best liquid phosphate bond.

(v) The strength increased with the increase in the amount of powder matrix and the corresponding phosphate bond.

(vi) **Very** high moulding pressure is not of advantage due to the bleeding of the liquid bond with the result that insufficient bond is left for reaction. The optimal

moulding pressure seems to be $800 - 1000 \text{ Kg/cm}^2$.

(vii) For maximum strength, the curing temperature is 800°C , since at both lower and higher temperatures the strength drops.

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